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10 APRIL 1987

JAPAN REPORT SCIENCE AND TECHNOLOGY

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DEVELOPMENT OF SHUTTLE VECTORS AMONG HETEROGENIC YEAST SPECIES

Tokyo BIO INDUSTRY in Japanese Aug 86 pp 14-21

[Article by Ichiro Shibuya and Minoru Morikawa, members of the Production Technique Research Institute of Nikka Whiskey Co., Ltd.; Shinya Kawai, member of the Department of Agriculture of Tokyo University; Masamichi Takagi, assistant professor of the Department of Agriculture of Tokyo University; and Keiji Yano, professor of the Department of Agriculture of Tokyo University; first paragraph is editorial introduction]

[Text] *Candida maltosa* is a yeast with an extremely unique property capable of resource-generating n-alkane, and by utilizing the Autonomously Replicating Sequence (ARS), which is the derivation of this yeast, the triple shuttle vector capable of performing the exchange of genes among the *C. maltosa*, *Saccharomyces cerevisiae*, and colon bacterium has been completed. In addition, the separation of the cycloheximide resistant gene of *C. maltosa* succeeded at the same time. The tasks of integrating these genes in plasmids and making improvements were attempted. It can be expected that these plasmids will be highly serviceable for genetic recombination.

1. Introduction

Yeast is an important organism in the fermentation and food industries, and today the establishment, application, and development of more useful strains are being attempted by using the DNA recombination techniques. One of the problem points when applying the genetic engineering techniques of yeast lies in discovering vectors necessary for integrating genes freely into the strain body. Many types of vectors have already been developed for *Saccharomyces cerevisiae*, which is a general specie among yeasts. However, vectors for other types of yeast are still few in number. Moreover, for promoting the utilization value of vectors industrially, they must be designed so they can come and go freely among the various types of yeast.

Lately, while conducting research on the n-alkane metabolic system of *Candida maltosa* with an extremely unique property capable of resource generating n-alkane, we were able to develop a shuttle vector capable of transforming *C. maltosa*, *S. cerevisiae*, and colon bacterium (Figure 1). Furthermore, since we were also able to newly isolate the cycloheximide resistant gene as the gene marker of the vector, we wish to introduce the experimental results and applications.

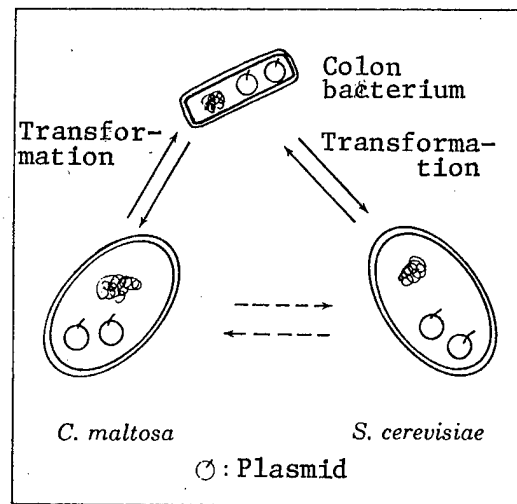


Figure 1. Triple Shuttle Vector

2. Basic Design of Vectors

The following various points can be considered to be the general conditions required for vectors.

- (1) Performs self-replication within the host and is maintained in a stable condition.
- (2) Either the host has a suitable transformant selective marker and a gene complementing this is integrated in the vector, or a gene providing a new character (for example, drug resistance) to the transformant is integrated in the vector.
- (3) There is a suitable cloning site in the vector and the insertion and freeing of exogenotes can be easily performed.
- (4) Replication is possible within the colon bacterium for the amplification and recovery of vectors.

In *C. maltosa*, which we used in the n-alkane metabolism research, a plasmid as in the case of *S. cerevisiae* could not be discovered. Therefore, the DNA interior core fragment Autonomously Replicating Sequence (ARS) which possessed the self-replication ability to replace this plasmid was isolated which was made a basis for utilization. Furthermore, from the fact that the leucine demand of the *C. maltosa* was complemented by LEU 2 of *S. cerevisiae*, it was used as a selective marker of the transformant. For the abovementioned conditions of (3) and (4), it was decided to use the minimum necessary part of vector pBR 322 of the colon bacterium in its generally used condition today.

3. Preparation of New Shuttle Vectors

Hereinafter, the preparation method of new vectors will be explained in order.

3.1. Isolation of ARS

Originally, the performing of self-replication within a host and the maintenance of stability are two different things, but the objective is generally achieved by isolating ARS into several parts and selecting the stable one from among these parts. The isolating method of ARS is shown in Figure 2.

First, all DNA were extracted from *C. maltosa*, partial decomposition was made with the restricted enzyme *Sau 3 AI*, this was ligated with the *Bam HI* site of *YEp 13* containing *LEU 2*, and a gene library was prepared. The leucine demanding *C. maltosa* J288 strain was subjected to transformation at this gene library and the leucine nondemanding strain was isolated. We must pay attention here to the fact that the 2 μ m DNA derived *Ori* of *S. cerevisiae* which is integrated in *YEp13* does not function in *C. maltosa*. Therefore, the leucine nondemanding transformant separated by the method shown in Figure 2 sometimes contains ARS derived from *C. maltosa*.

Under such a method, plasmids were separated from several colonies having a superior growth, the most stable plasmid was selected from among these plasmids, and *pCS 1* was obtained. The restricted enzyme map of *pCS 1* is shown in Figure 3. Moreover, a protoplast method, such as the Hinnen method, was used in the transformation of *C. maltosa* based on the case of *S. cerevisiae*.

Then, a subcloning was performed on this ARS part and the range (TRA range) of about 3.8 Kb was isolated (Figure 4).

3.2 Preparation Method of New Shuttle Vectors

As a DNA piece having a self-replication capacity, the aforementioned *pCS 1* vector possesses two ranges, TRA and *Ori* of 2 μ m DNA. If the TRA range also functions in *S. cerevisiae* and not only in *C. maltosa*, *Ori* of 2 μ m DNA will become unnecessary. Thereupon, the construction of new shuttle vectors was attempted. The procedures are as shown in Figure 5. The necessary ranges are the TRA ranges and *LEU 2* gene and the *pBR 322* derived piece are necessary. The following were the construction procedures adopted.

- (1) After the scission of *pCB 1* with *Bam HI*, the TRA range of about 3.8 Kb was separated and made the smoothing terminal.
- (2) After the scission of *YEp 13* with *Bgl II*, the *LEU 2* gene was separated and made the smoothing terminal.
- (3) After the scission of *pBR 322* with *EcoR I*, it was made the smoothing terminal.

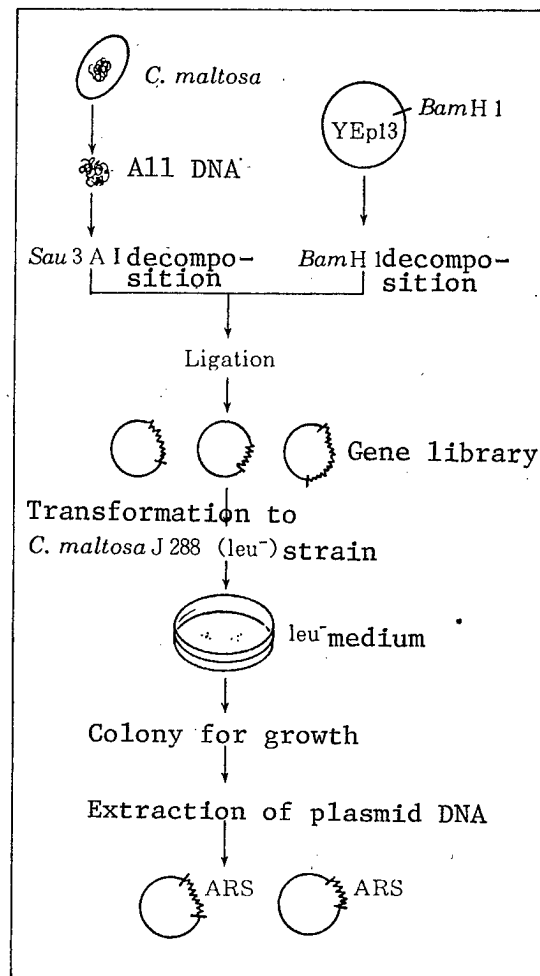


Figure 2. Isolation Method for ARS of *C. Maltosa*

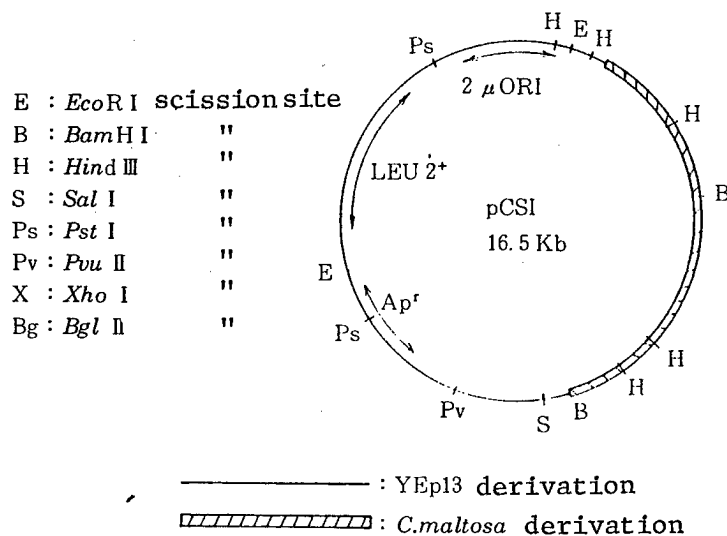


Figure 3. Restricted Enzyme Map of Plasmid pCS 1

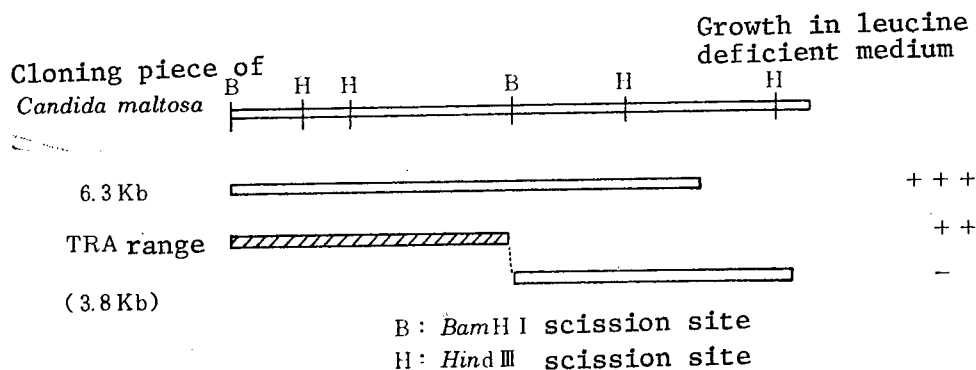


Figure 4. Subcloning of Plasmid pCS 1

(4) A smoothing terminal linkage reaction of the LEU 2 gene obtained in procedure (2) above was performed at the *Eco*R 1 scission site of pBR 322 mentioned in procedure (3) above and pIL 1 was prepared.

(5) After the scission of pIL 1 with *Xho* I, it was made the smoothing terminal.

(6) A smoothing terminal linkage reaction of the TRA range obtained in procedure (1) above was performed at the *Xho* I scission site of pIL 1 mentioned in procedure (5) and pTRA 1 and pTRA 11 with the TRA range insertion direction mutually in the opposite direction were prepared.

3.3 Properties of the Shuttle Vector

Next we will explain the properties of this vector. The restricted enzyme map is shown in Figure 5.

(1) The size is about 11 Kb.

(2) Cloning site

As shown in Figure 5, the vector has a total of two cloning sites. One site is *Bam*H I within the tetracycline resistant gene and the other is *Pst* I within the ampicillin resistant gene.

(3) Selective marker in the colon bacterium

The ampicillin resistance and tetracycline resistance.

(4) Selective marker in the *C. maltosa*

The leucine demand of the *C. maltosa* J288 strain is complemented.

(5) Transformation frequency in *C. maltosa*

When a protoplast method such as the Hennen method is used, transformants of about 1,600 each per DNA 1 μ g are available and this is a sufficient

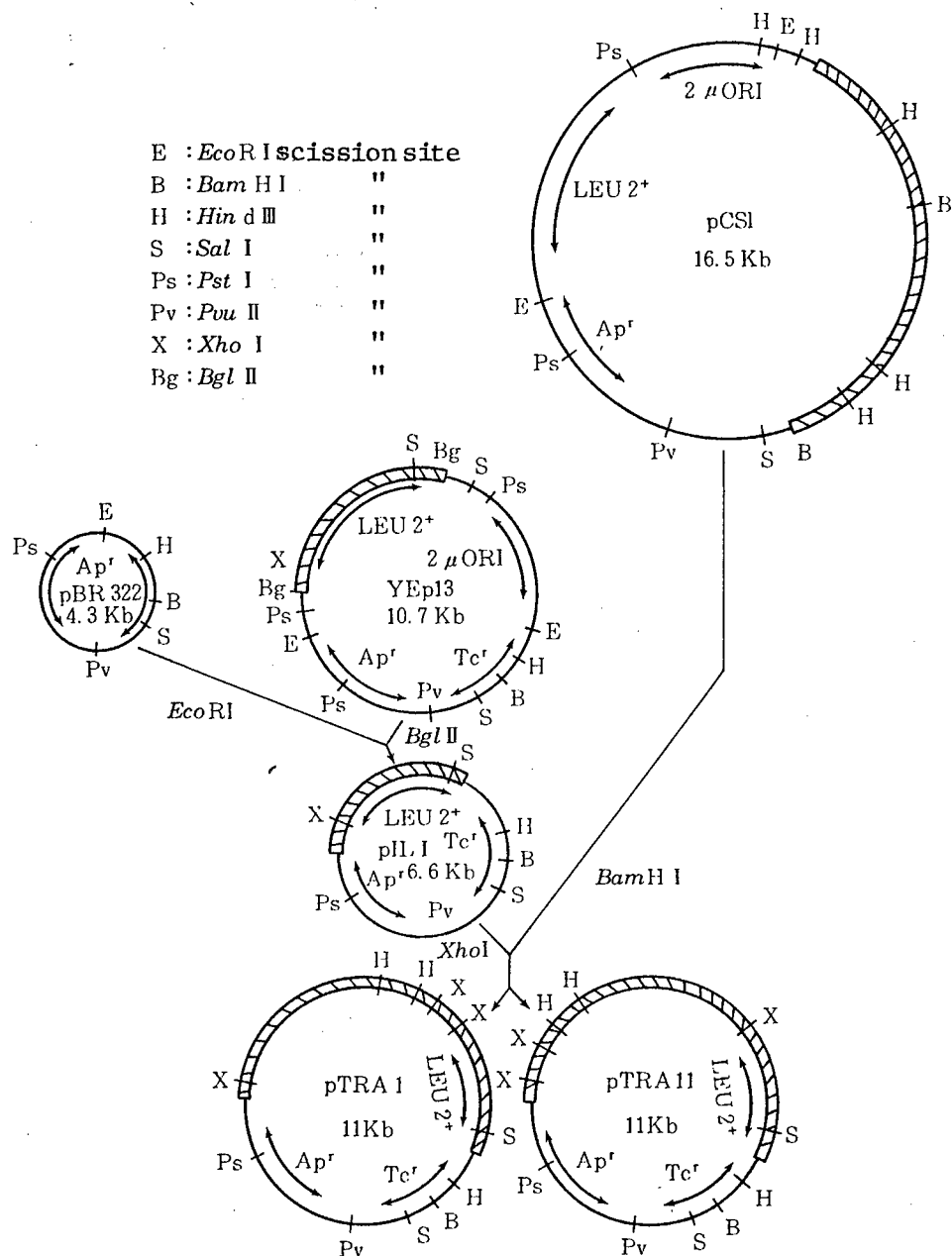


Figure 5. Preparation of New Shuttle Vector

frequency for an ordinary cloning experiment. On the other hand, the lithium metal method is also a transformation method of *S. cerevisiae* and for reasons such as operation simplicity and isolation ease of the transformant, this method has spread rapidly in recent years. Upon using this method for the transformation of *C. maltosa*, we were able to obtain transformants of about 500 each per DNA 1 μg and it became clear that this method was an extremely powerful means.

(6) Stability of plasmid

Next, upon performing research on the stability of plasmid, both pTRA 1 and pTRA 11 were considerably stable even after performing a 15 generation culture by a complete nutrient broth without selective pressure.

(7) Transformation to *S. cerevisiae*

No matter whether the protoplast method or lithium metal method is used, transformants of about 300 to 3,000 each per DNA 1 μ g are available, and it has been confirmed that it adequately functioned as an ARS (Table 1). Thus, it became clear that it was a shuttle vector which worked among the *S. cerevisiae* and colon bacterium as well as the *C. maltosa*. The main properties of this vector are shown in Table 2.

Table 1. Transformation Frequency of Vectors

	Transformants per DNA 1 μ g		
	Protoplast method		Lithium method
	<i>S. cerevisiae</i>	<i>C. maltosa</i>	<i>C. maltosa</i>
YEp 13	820	0	0
pTRA 1	3,080	1,650	510
pTRA 11	920	460	60

Table 2. Main Properties of New Shuttle Vectors

Property	pTRA 1 or pTRA 11
Size	10.1 Kb
Cloning site	BamH I, Pst I
Marker in colon bacterium	Ampicillin resistance Tetracycline resistance
Marker in <i>C. maltosa</i>	Complements leu ⁻ (J288 strain)
Marker in <i>S. cerevisiae</i>	LEU 2

4. Cycloheximide Resistant Gene

Generally, the presence of nutrient demand is utilized for checking whether or not the yeast has been subjected to transformation and whether or not the intended gene has been introduced. However, this type of method cannot be used in the case of a wild-type strain which does not indicate a nutrient demand. In the *S. cerevisiae*, the G418 resistant gene, DHFR gene, and copper

resistant gene (CUP 1) are presently known as genes having drug resistance. Upon considering whether or not the cycloheximide resistance possessed by *C. maltosa* could be used as the selective marker, we attempted the isolation of the resistant genes.

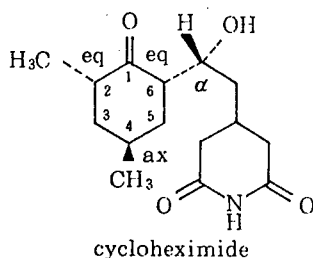


Figure 6. Molecular Structure of Cycloheximide

The cycloheximide (Figure 6) is one of the glutalimide antibiotics. Its functional actions such as bonding to the 60S ribosomal subunit of an eucaryote and inhibiting the elongation reaction of protein synthesis are known. Practically all eucaryotes including animals and plants have a sensitivity against cycloheximide. The *S. cerevisiae* is no exception and it is not able to grow in a medium containing cycloheximide with a concentration of more than 0.1 $\mu\text{g}/\text{mL}$. However, several *Candida* genus yeasts, as well as *C. maltosa*, possess a cycloheximide resistance and in the case of *C. maltosa*, growing in a medium containing cycloheximide with a concentration of more than 1 mg/mL is possible and it is known that its resistance mechanism is inductive.

Here, explanations will be made of the isolation method of the cycloheximide resistant gene and its properties.

4.1 Isolation of Cycloheximide Resistant Gene

The isolation method of the cycloheximide resistant gene is shown in Figure 7. The gene library used here is the same as that used when isolating ARS.

(1) A transformation is performed on the *S. cerevisiae* AH 22 (leu^-) strain by using the gene library of *C. maltosa* and the transformation strain is selected by the leucine deficient medium.

(2) The transformation strain is replicated in a YPD nutrient broth containing cycloheximide (1 $\mu\text{g}/\text{mL}$), and after its culture the cycloheximide resistant strain is selected.

(3) DNA is separated from the cycloheximide resistant strain and after amplifying with colon bacterium, the cycloheximide resistant gene is separated.

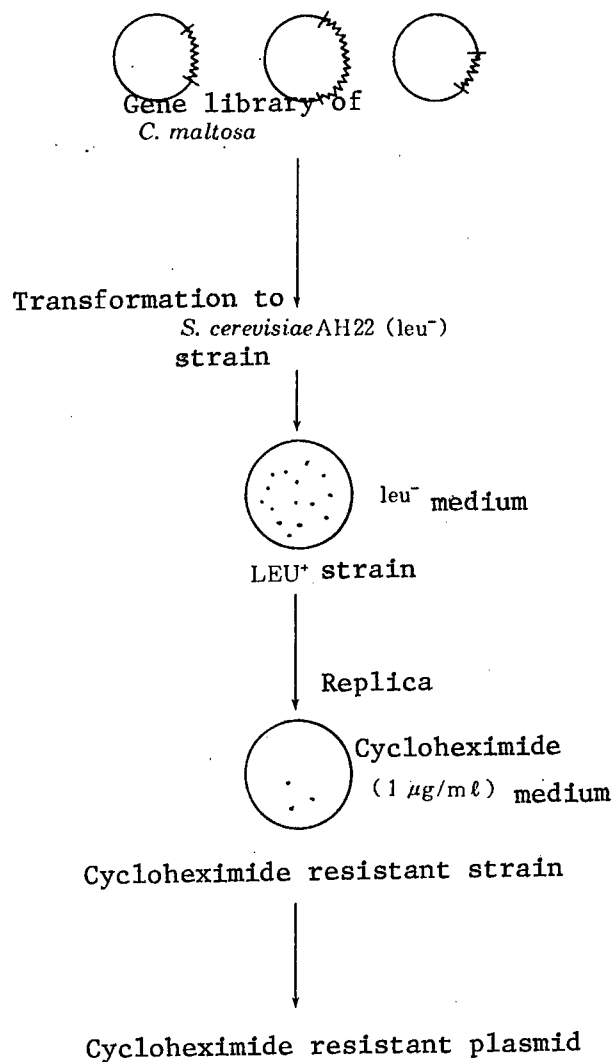


Figure 7. Isolation Method of Cycloheximide Resistant Gene

The abovementioned procedures are for isolating the cycloheximide resistant gene.

Several resistant plasmids were obtained by this method and by making one of them the pRIM-C, it was used for the following analysis. In pRIM-C, the DNA range derivated from the *C. maltosa* containing the resistant gene was about 4.3 Kb but it was reduced to about 1.1 Kb by subcloning and pRIMC-201 was obtained (Figure 8).

4.2 Applications as a Vector Marker

We are presently analyzing the cycloheximide resistant gene product which has been subjected to cloning, and there is a possibility of it being a ribosome subunit or a modification enzyme. The mechanism of how it becomes

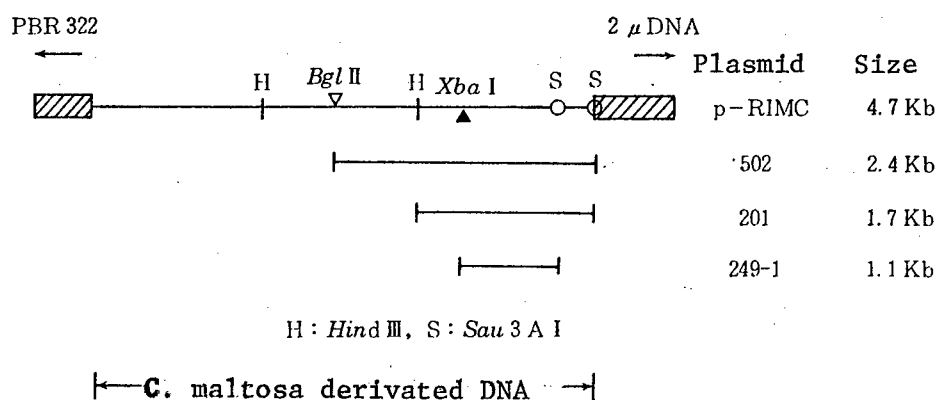


Figure 8. Cycloheximide Resistant Gene

resistant is not yet known, but the use of this gene as the selective marker of the transformant is extremely effective. Mention will be made in the following of the properties of this gene and examples of its application.

(1) Cycloheximide resistant concentration

Upon investigating the extent of cycloheximide concentration a plasmid having a cycloheximide gene which has been subjected to cloning can withstand, it became clear that it can grow sufficiently even in a medium containing a high concentration cycloheximide of more than 1 mg/ml. From the fact that the growth of a normal *S. cerevisiae* can be completely checked at a concentration of 0.5 μg/ml, it is considered to be sufficient as a marker.

(2) Manifestation of cycloheximide resistance in various plasmids

Next, we relinked the cycloheximide resistance gene to other vectors besides the YEp type and studied the relation with the cycloheximide resistance manifestation. The result is shown in Table 3. As comprehensible from this table, the cycloheximide resistance was not available in the YIp type YCp type vectors with a small number of copies and the gene dosage effect was observed in the cycloheximide resistance.

Table 3. Vector Type and Cycloheximide Resistance

Plasmid	502	224-2	223-1	268
Vector	YEp 13	YRp 7	YCp 19	YIp 33
ARS	2 μ Ori	ARS 1	CEN 4	Integrated
Number of copies	50~100	5~10	1	1
Cycloheximide resistance*	+	+	-	-

* Judged in YPD medium containing 1 μg/ml of cycloheximide.

+ : Possesses resistance
- : Does not possess resistance

(3) Direct Selection in the Wild-Type Yeast

As we have already mentioned, the greatest utilizing purpose of the cycloheximide gene lies in the direct selection of the transformant. Therefore, we used the plasmid pRIM-C201 and performed a transformation by making the laboratory used wild-type diploid as the host. The lithium method was initially used, but a stable transformant was not available. Thereupon, by modifying the conventional protoplast method and multilayering the medium containing drug during the regeneration, transformants of 100 to 1,000 each per DNA 1 μ g were available.

(4) Application to Other Eucaryotes

As aforementioned, practically all eucaryotes have a sensitivity against cycloheximide, and animals and plants are no exceptions. On the other hand, several drug resistant markers are presently known as vector markers of animals and plants (for details, see the other theories) and we are performing research upon considering that the isolated cycloheximide might be applicable as a vector marker for animals and plants. Although there are many unknown parts in the vector of animals and plants, we believe that research results in the future harbor great expectations.

5. Conclusion

We have explained the preparation of ARS containing pTRA 1 and pTRA 11 of *C. maltosa* and have recently also constructed new vectors integrating a cycloheximide resistant gene in these shuttle vectors. Research is presently being done on the extent to which these vectors can be used for wild-type yeasts. Moreover, we are considering improving these vectors in the future so they can also become applicable to the cell system of animals and plants as well as yeasts. We hope that such new vectors will be serviceable for the yeast and food industries.

The contents of this research were the main points of the invitational addresses (Masamichi Takagi, et al.) made public at the 10th International Yeast Special Symposium (held in Bulgaria in 1985), including those not yet made public.

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BIOTECHNOLOGY

FUSION OF BIOTECHNOLOGY, ELECTRONICS DISCUSSED

Tokyo BIO INDUSTRY in Japanese Aug 86 pp 54-59

[Article by Tsuguchika Kaminuma, Tokyo Metropolitan Clinical Medicine Integrated Research Institute; first paragraph is editorial introduction]

[Text] Amalgamation of biotechnology and electronics is not simply the amalgamation of both techniques but should be the amalgamation of life science and computer science that underlie these techniques. The interchange of these two branches of science occurred once around the time of the birth of the computer but ended in a barren incident. This was due to the fact that the understanding of life in terms of the basic principles was lacking. Understanding life in terms of basic principles should play a central role in the new interchange.

1. Introduction

"Electronics that are located in the center core of biotechnology will merge to create new technology fields which become the foundations of the next generation's industrial society."

The author wrote a book exploring the future of biotechnology and the computer. The title of the book is "Biocomputer." The book, however, does not contain much description about "the biocomputer" itself.

According to the author's definition, a biocomputer has distinctive features of a living organism. A biocomputer is the symbolic point at which the new technology through the amalgamation of life science and computers or that of biotechnology and electronics converge. It is by no means likely that biocomputers as shown in the picture can be constructed immediately. It is a matter of time, however, when research aiming at biocomputers gets started.

In the following, the author will explain the reason why he thinks biotechnology and electronics will merge in the near future and consider the significance of the amalgamation and how to tackle this problem.

2. Historical Consideration

In nature, biotechnology has a deep relationship with electricity. Physiological experiments, in particular, have been intimately tied with electrical technology. It was also physiologists who made contact with electricians/

mathematicians around the advent of the computer. Norbert Wiener, an advocate of cybernetics, famous along with (Shannon) Wiener's information about measuring the amount of information in terms of entropy function have long collaborated with Bruce Rosen, a medical physiologist. A neuronal circuit network known as a perceptron (also to technologists) was proposed by a psychologist, (Rosenblat). The proposal was based on the neuron model by physiologists, McCulloch and Pitts. At that time, it was an initial time of getting to know each other with computer researchers and physiologists, respectively, regarding opponents as partners with the intention of exchanging ideas.

In spite of the fact that the term cybernetics became popular, the dialogue between computer researchers and physiologists was not proceeding smoothly. Computer researchers, in particular, did not get any hints for developing computers from physiologists. Likewise, physiologists did not get hints for performing their research directly from computer/electronic researchers.

The advancement in instruments fortified with electronics helped medical physiologists a great deal. It was viewed that electronics researchers were sellers of the technique and medical physiology researchers were their buyers. The market was called living organism technology, the technology for medical use, or electronics technology for medical use.

From these interchanges, two generally applicable techniques, particularly worth mentioning, were born. The first is the computer tomography commonly called CT and the second is the artificial intelligence system (expert system). The mathematical principle of CT had already been discovered by the mathematician (Radon) at the beginning of this century. It became possible, however, only with the aid of the computer that the data obtained by repeated linear radiation-scannings was converted into the two-dimensional distribution of absorption coefficients. Expert systems can automatically make decisions instead of man on the basis of knowledge of so-called experts such as organic chemists, analytical biochemists, and physicians, etc., collected and stored in order and are now very fashionable. Either of these techniques emerged in the period from the latter half of the 1960s to the first half of the 1970s.

In addition, the term "bionics" came to be used from the beginning of the 1960s. This approach started from the wish of technologists to learn from living organisms. How far bionics has been pursued is beyond the author's understanding. The interest of technologists was directed toward various subjects such as the eye of frogs, supersonic radar of bats, zigzag-wavy motion of snakes, and the high speed submarine swimming style of dolphins. None of the results, however, deserve the name of bionics to say nothing of the impact on the computer. It is not in technology but in biology that research having dealt with living organisms in laboratories made contributions.

The technology concept of a marriage between biotechnology and electronics which is spoken of today has been advocated since the onset of the 1980s. Since then, the orbit of the interchange between life science and the

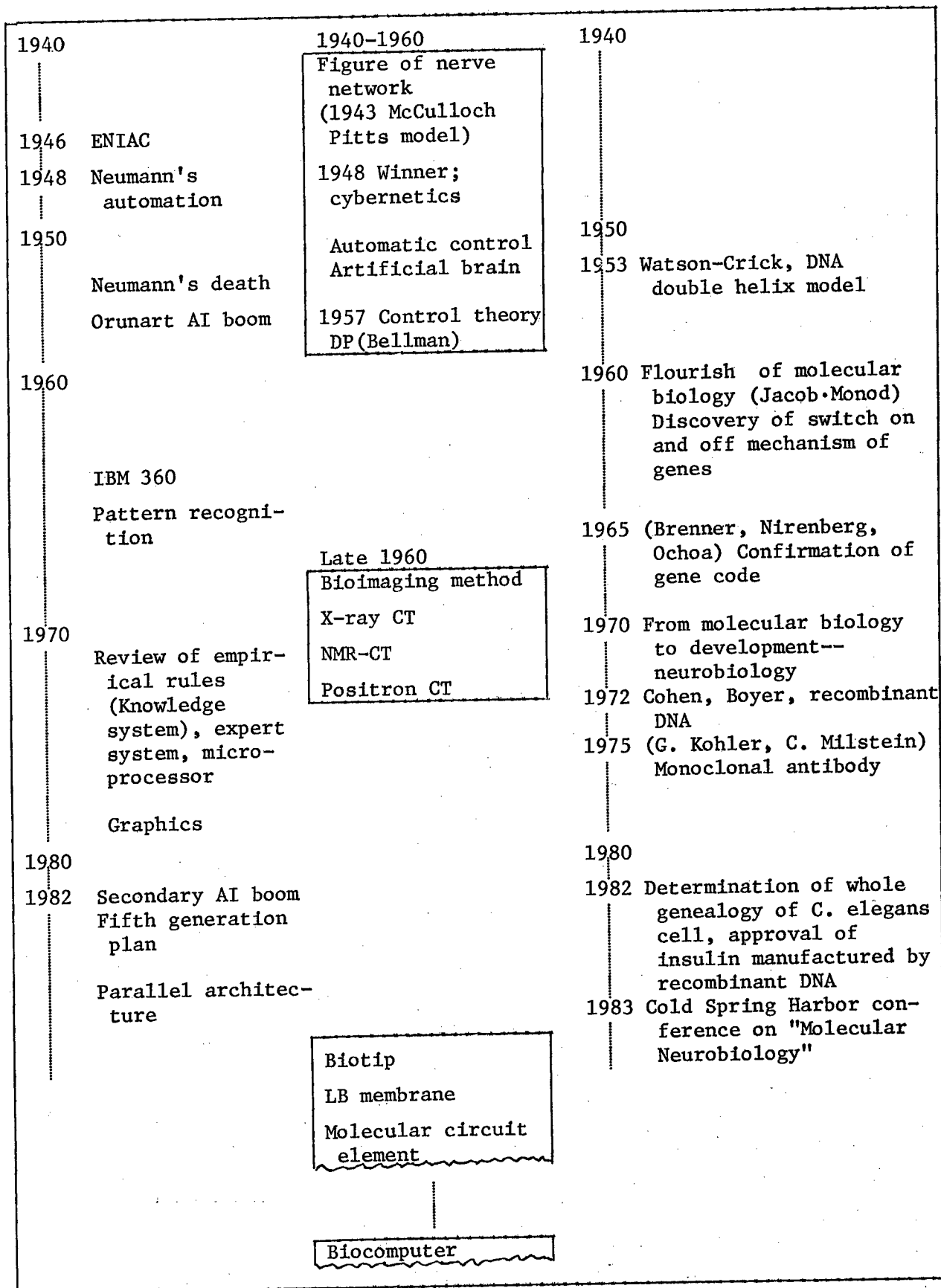


Figure 1. Interchange of Computer and Life Science or Biotechnology [Table 2 in Reference 1 was modified]

computer have been clearly recognized. The pursuit of an analogy between neurophysiology and technological circuit networks, measurement technology in living organisms and bionic approaches are still continuing at present.

Technology on bioorganisms directly connected to electronics such as X-ray (CT), nuclear magnetic resonance, positron CT, the combination of monoclonal antibodies and imaging technology dry chem (easy-to-handle blood test) and biosensors, in particular, are the fields where the most prospective advances are anticipated. Medical science will make epoch-making progress in accordance with the advances in these measurement technologies and biology will receive a great boom as well.

Measurement technology in bioorganisms, however, should be regarded as applied techniques and not the amalgamation of biotechnology and electronics itself. Only biosensors are one of the few exceptions.

3. Prerequisites for New Technology

In my personal view, the real merge of electronics and biotechnology is yet to get started. New techniques deserving the name must be essentially different from the cybernetics, bionics/measurement technology of bioorganisms encountered so far.

The grasp of living organisms was only fragmentary, superficial and in a "black-box" fashion in the interchange of life science (biotechnology) and computer (electronics) technology as experienced so far. Technologists attempted to make machines resembling living organisms, but it was difficult to find a mechanism which technologists were interested in using. For example, even if the resemblance of the regulatory mechanism in the cerebellum to the perceptron was discovered, technologists already put into allegorisms far more complicated recognition mechanisms than perceptrons. The ideal case in which a biological discovery was hinted at directly to technologists has never materialized.

It has been nearly 40 years since "cybernetics" was published by Winner, and it has been more than 20 years since cybernetics was advocated for the first time. We have to consider the fact that research along this line did not lead to as fruitful results as expected both in applied and basic research.

The reason why such an approach resulted in the betrayal of our expectations can be explained by the following sentence. This is because the living organism was not understood in principle. The approach to learn from living organisms will not produce good results and perhaps prove futile unless living organisms are understood in principle terms. This is a precious lesson we have learned. In order to keep this lesson effective, one has to be loyal to the justifiable idea in research that the first thing to be done is the elucidation of the principles of living organisms when the development of technological machines is intended based on what is learned from living organisms.

Many readers, however, will refute this, saying it is not easy to elucidate the principles of living organisms. This is because unlike physics or chemistry, biology continued to be just descriptions of phenomena in living organisms and not sophisticated to the hierarchy of science. It has been since 1950 that biology established its basis as a science. In that sense, biology is a young science that has just been born. The fact that in contrast to the thriving in chemical or physical societies the academic society of biology does not exist in Japan even at present.

Furthermore, it was the middle 1970s when gene engineering based on scientific principles got started and only 10 years has elapsed since then. It has been only 5 years since it made inroads into Japan. Propagation speed of technology during this period, however, is certainly marvelous and the increase in knowledge obtained by making technology available threatens to explode.

When this situation is viewed from the standpoint of technologists, it may be said that the approach to obtain technological hints by studying living organisms on the basis of principles is becoming realistic after a rather long-time lag. Now technologists are confronted with the choice between two alternatives. One is to concentrate developmental research depending on the principles biologists established and the other is to have themselves more involved in biology to elucidate biological principles before they can be applied.

When the R&D systems are viewed as a whole at the national level, both approaches are being undertaken. Which approach to choose depends on the intention of the individual researchers and the situations they are put in, so it is not a matter for criticism from outsiders. Generally speaking, the research system in the electronics sector will have to step deeply into the domain of biology.

4. Scientific Climate and Soil in Japan

Why is this so? The reason is very simple. This is because in Japan, the level of technology such as physicochemical analysis, biochemistry, and fermentation analysis of living organisms as substances and utilizing them is high, but methodology inherent to biology that analyzes living organisms in terms of being "things" as in the case of genetics is weak. That is to say, Japan's biotechnology is based on biology in terms of substances, and not considered in terms of "things." Also, this is why Japan hardly contributed to the birth of molecular biology. Of course, there are quite a few Japanese who contributed to molecular biology; most of them, however, were in the research group abroad.

It has continued to be the trend of biology (or science in general) in Japan that research in the frontier fields is inert. Private enterprises began investing in basic research abroad to circumvent the risk in R&D dependent on Japanese biology. Probably they think that is cheaper and more efficient as well.

This is not a good trend. Indeed, the opinion is frequently heard that basic or creative research should be encouraged. Actually, such an investment is intended to be a substantial part of the capital invested there, however, it is engulfed in the reinforcement of the research Japan is best at. That is to say, the money is used for research expenses for "orthodox" researchers with an already established reputation. It is also true that these investments are not so effective as they are intended to be if not futile. The case applies not only to life science or biotechnology but also to computer science.

If new science and technology are to be pursued, it is no use relying on the project at the mercy of the men of ability who have been manifesting executive power within the already established evaluation system belying the words on the signboard saying "creative" or "original."

If it is reiterated for the sake of avoiding misunderstanding, such climate and soil are suited to "come from behind catch up and go ahead" type science or technology, which may not be necessarily entirely negated. This approach, however, cannot afford to exploit a new field such as the interdisciplinary domain between life science and computer science. The only thing it can do is to keep fighting the come from behind game Western countries set up. If it is desired that R&D in our country leads the world from the beginning, each private enterprise will be required to propel basic research under long-term vision. Enough capital is already available to do so, and it is not difficult to collect capable scientists either. It is only research strategy and management, i.e., that need to be pursued and the approach that is difficult.

5. What Should Be Borne in Mind With Respect to Research Strategy?

The author has been engaged in the very practical work of the improvement of medical care for the last 15 years and has been tied directly neither with the life science (biotechnology) nor with the computer (electronics). This helps the author to look at the situation from a distance. The following discussion should be read with a saying in mind that goes, "the outsider sees the best of the game."

First, what appears to be very strange is the fact that many R&D institutions, enterprises in particular, converge on similar subjects. Interferon in the first biotechnology boom and biosensors in the exalted mood of "bioelectronics" are typical examples of this trend. Even if these targets are attained, the market sizes are limited. Suppose acquisition of the technique is the objective, whether acquisition of such stereotyped techniques is meaningful or not is questionable.

Second, philosophy is lacking for wrestling with basic research. The author once heard of an extreme case in which the first year was scheduled for basic research and the second year for development of the product. It is even humorous rather than surprising to know that this is the limitation a major electronics maker imposed on their adopted researchers. Whatever hardship the company may be confronted with, severity proves itself only under a

well-defined philosophy. Casual measures for the sake of convenience will only deprive talented men of opportunity.

Conversely, there are some cases of having adopted some researchers in the basic field and leaving them alone. Without having objectives to pursue, such researchers may well indulge themselves in presenting meaningless papers to the academic meeting or preparing manuscripts to be submitted for publication.

If basic research is to be promoted, the target should be focused on the important fields and fine talented men should be selected for the project and backed up intensively.

What type of field should be selected as the target, then? From the standpoint of electronics-- 1) science of biopolymer, protein in particular; 2) development of multicellular organisms and morphogenesis; and 3) nervous system--brain science can be considered. There could be other fields that are important. They are, however, not at the frontier of life science and therefore would be incompatible with computer (electronics) makers.

The next problem will be what kind of biological material should be selected. The maintenance and control of experimental animals are cumbersome and costly. Therefore attention is paid to minute or miniature animals that are convenient for rearing, culture, and line control. For the monoclonal antibody, however, larger animals have to be used although many are not necessary. Rooms for experimental animals will have to be prepared after all even if small in scale.

Next in importance is to make the best use of computers in developing research. The author has opportunities to hear stories of people from various enterprises such as pharmaceutical, chemistry, materials, and electronics. According to these sources, the availability of computers for research is surprisingly poor. Similar situations apply to universities and national research institutes. This means a loss in a dual sense. First, the efficiency of the research is low for the time being. Second, important opportunities for dialogue between the experts of life science and those of computers are being lost.

A latter problem is also important from the viewpoint of the amalgamation of biology and electronics and will be discussed a little more in detail.

6. New Dialogue Between Life Science Scientists and Computer Technology Scientists

Molecular biology that conferred scientific basis on biology clarified the remarkable fact that living organisms were chemical computers having a programming tape of nucleic acid chains. Computers and life science are both digital information machines. This very fact is the most reliable evidence for the prediction that biotechnology and electronics or life science and computers will coalesce in the future.

Now research in both fields has a basis on which they can debate on equal terms getting back to the architecture of life and the computer. Life science and biotechnology are not merely the market or users of computers to the computer people anymore. Conversely, to life science and biotechnology researchers, computer experts are not only the convenient beings by whom life science and biotechnology researchers get data processed but also they are becoming partners with whom science can be discussed together.

The dialogue held among mathematicians, circuit technologists and nerve physiologists around the time of the birth of the computer will have to be expanded and taken over by molecular biologists, biochemists, chemists, and computer technologists. Furthermore, immunologists, developmental biologists, nerve biologists, brain scientists, and physicists will shortly join this dialogue.

Real amalgamation of biotechnology and electronics is not the merge of the technologies but the merge of the sciences that underlie them. That this merge is an inevitable consequence is what the history of science had demonstrated. The remaining task will be how it is embodied concretely at the science and technology level. This, however, will depend on how the merge is developed. What the author wishes to say is that the key point is the attitude of computer specialists in the research field of life science and biotechnology.

This author proposes not to label computer specialists in this field as servicemen taking care of computers but to gather theoretical specialists studying the biological architecture ranging from the molecular level to the multicellular systems and the brain and have computer specialists in the core of the research project supported by these scientists. The author thinks this will become a first step in the true amalgamation of biotechnology and electronics research. Would such a view be too personal and distorted? The author would like to leave the answer to the readers.

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NEW MATERIALS

RESEARCHERS SEEK WAYS TO PRODUCE TOUGHER CERAMICS

Dispersion Toughening

Tokyo CERAMICS JAPAN in Japanese Jul 86 pp 605-612

[Article by Noboru Miyata, lecturer on engineering at Kyoto University]

[Text] 1. Introduction

Researchers have long worked to produce a ceramic of higher toughness and, as a consequence, it has been established that, since as raw material ceramic is by nature brittle, the dispersion or deposition of a non-homogeneous phase in the raw material phase is effective in dissipating fracture energy. Intensive research is being promoted to discover the condition that permits creation of ceramics of high strength and high toughness on the basis of known mechanisms for improving toughness of the material. This paper presents a summary of the basic research so far accomplished in connection with the toughening of ceramics by means of particle dispersion.

2. Factors Influencing the Strength of Ceramics Toughened by Particle Dispersion

Ceramics toughened by particle dispersion may be regarded as a composite material which involves one or more dispersion phases in its brittle matrix. The mechanical properties of this type of composite materials are dictated not only by those of the constituent phases but also by various composite effects in large measure, e.g., additive-property effects, structural effects, and interface effects.¹⁾ In terms of the composite effect, the composite materials of a brittle matrix with particles dispersed above have their strength characteristics governed generally by the following factors:

- 1) Conditions in which the dispersed particles are combined with the matrix at the interface.
- 2) Discrepancy between the properties of the dispersed particles and those of the matrix, e.g., differences in thermal expansion coefficient, ones in elastic modulus, and ones in toughness or in fracture energy.

3) Geometrical factors, e.g., size of dispersed particles, shape of the particle, stance among dispersed particles.

Percentage in volume of the particle, and distribution of the particle.

In cases where the matrix is made up of polycrystals, the size of these particles relative to the dispersed particles and the position of the particles of the dispensed second phase (whether the particles are in the boundary area of the matrix particle or in the matrix particle) also poses important questions.

3. Theory for the Strength of Ceramics Toughened by Dispersion

The stress, σ_f , required for the fracture of a brittle material, according to the fracture criteria of Griffith,²⁾ are given by

$$\sigma_f = \frac{1}{Y} \sqrt{\frac{2\Gamma E'}{c}} \quad (1)$$

where c denotes the size of the critical crack for the development of unstable fracture, Γ fracture energy, and Y a dimensionless constant dependent on the shape of the object and the crack. E' , in turn, is given by either

$$E' = E \text{ (in plane stress conditions)} \quad (2)$$

or

$$E' = E/(1-\nu^2) \text{ (in plane deformation conditions)}$$

where E stands for Young's modulus and ν Poisson's ratio. Alternatively, σ_f may be represented in terms of linear fracture mechanics³⁾ as

$$\sigma_f = \frac{1}{Y} \frac{K_{Ic}}{\sqrt{c}} \quad (3)$$

where K_{Ic} stands for the critical stress intensity factor and

$$K_{Ic} = \sqrt{2\Gamma E'} \quad (4)$$

where Γ and K_{Ic} are both constants specific to the raw material and represent the resistance of the raw material against brittle fracture; they make measures of the work necessary for the fracture of a raw material and may hence be regarded as the parameters of its "toughness." The K_{Ic} , in particular, is referred to as fracture toughness and used frequently as a measure of toughness for the sake of practical convenience.

In connection with the increase (or decrease) of strength resulting from dispersion of a second phase in a brittle matrix, the following two fundamental mechanisms have been suggested:

1) The size of cracks specific to a raw material is changed by the presence of particles of the second dispersed phase.

2) The second dispersed phase either blocks or helps the extension of cracks, i.e., it produces a change in fracture energy.

The theories for the strength of ceramics involving a dispersion of tough particles therein are represented by that of Hasselman⁴⁾ et al., based on the above mechanism (1) and by that of Lange⁵⁾ based on the mechanism (2).

The theory of Hasselman, et al., assumes that, as the distances among dispersed particles become smaller than the size of cracks specific to the matrix, the size of cracks to be produced in the material becomes limited by the distance among the particles, leading to greater strength. This theory does not allow for the effect of the particle of the second phase on the fracture energy Γ . The Lange's theory, in contrast, infers that a direct reciprocal reaction between the extending main crack and a second-phase particle produces a rise in fracture energy and hence in strength of the material. The relationship between the size of critical crack c and relevant fine structures, however, has yet to be elucidated in this theory.

Harmonization of the above two theories of different approaches and hence completion of the theory of the strength of ceramics toughened by dispersion require elucidation of the mechanism by which microscopic cracks have been developed or interconnected before a macroscopic unstable fracture occurs.

4. Mechanism of Toughening Ceramics by Dispersion

Of various energy dissipating mechanisms involved in ceramics toughened by particle dispersion, the author deals here with crack bowing, crack deflection, and microcrackings, which work as the major mechanisms for improving the toughness of ceramics in many systems.

4.1 Crack bowing

This mechanism for enhancing toughness has been suggested by Lange⁵⁾ and Evans⁶⁾: The advance of a main crack is blocked by particles dispersed in the brittle matrix and the advancing front of the crack bent in semielliptical form between adjacent two particles, thereby producing a line tension effect, which, in turn, increases fracture energy and raises strength of the ceramic (Figure 1); the Lange-Evans theory, namely, postulates an effect similar to the line tension effect arising when a dislocation is bent between obstacles mingled. Lange represents the fracture energy of a brittle material involving a dispersed-particle phase by the formula

$$\Gamma = \Gamma_m + \frac{\tau}{d} \quad (5)$$

where Γ denotes the line tension of an advancing crack-front, d distance between particles, and Γ_m the fracture energy of the matrix. Evans advanced the Lange's theory further and estimated the contribution of the line tension effect to the increase of the toughness of the ceramic as a function of the ratio of the particle diameter to the distance between the particle by using a two-dimensional model like that shown in Figure 1.

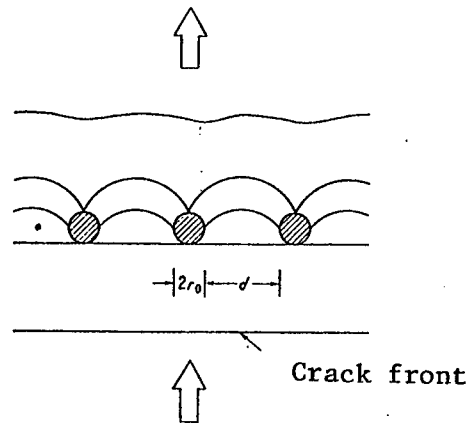


Figure 1. Bowing of the Crack Front Between Dispersed Particles

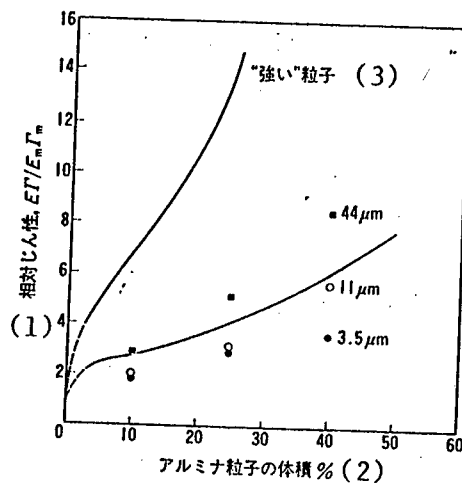


Figure 2. Changes in Toughness of a Composite Material Made of a Glass Matrix⁸⁾ and Alumina Particles, Together with Theoretical Curves Based on the Crack-Bowing Model⁷⁾

Key:

1. Relative toughness
2. Percent in volume of alumina particles
3. Strong particle

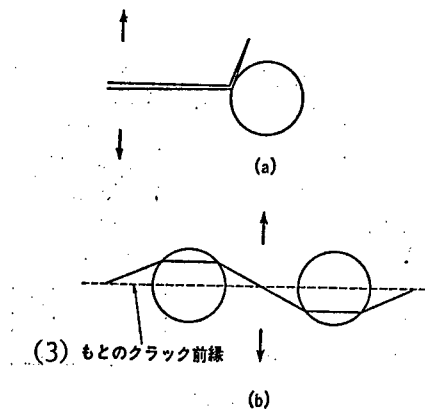
Theoretical treatment of the above mechanism initially involved the postulation of impenetrable obstacle or the postulation that the dispersed particle has toughness greater than that of the matrix and that the particle is capable of effectively blocking the progress of cracks without itself being destroyed or separated from the matrix before it has been surrounded by the crack; namely, the crack undergoes pinning temporarily. On the assumption of the presence of such a "strong" particle, the toughness of the ceramic must rise in a great measure with decreasing distance between particles⁷⁾; in cases where particles are destroyed before the advancing front of the crack is sufficiently bent and where the boundary between the matrix and particles is broken, however, the rise of the toughness of the ceramic is not as large as it is when the presence of "strong" particle is postulated. This implies that the contribution of the linear tension effect to the rise of toughness of the ceramic is dictated in a large measure by whether the particle works as a strong or weak particle and depends heavily on the difference between the toughness of the matrix and that of the particles, conditions of the boundary between the matrix and the particles, extent of the discrepancy in thermal expansion and various other factors.

Figure 2 shows a plot of the toughness⁸⁾ of a glass-matrix alumina-particle composite produced by means of hot pressing against percent in volume of its alumina particle, which Green⁷⁾ analysed using his crack-bowing model. This composite system does not involve a discrepancy in thermal expansion coefficient and hence a bowing of the main crack, conceivably, is the major mechanism accounting for the rise of the toughness of the ceramic with the alumina particle acting as a "weak one." Air bubbles and particles poorly bound to the matrix, meanwhile, are extreme examples of "weak particles;" it was revealed, nevertheless, that even these particles, when present in the matrix, produce bowing of the main crack and hence contribute to an increase in the toughness of the ceramic to a limited extent.⁹⁾⁻¹²⁾ Such a bowing of the main crack due to "weak particles" seems to result more from the blunting of part of the crack front encountering the dispersed particles than from the pinning of the front.

Figure 3 [omitted] is an electron-microscopic picture of a fractured surface of a composite material of glass matrix and spherical alumina particles studied by the author, et al., which indicates how a crack front undergoes bowing between the particles. The bowed crack fronts, as they leave the particles, collide with each other and form characteristic surface steps. The postulation that the crack front involves a linear tension has been objected by some and the nature of the crack bowing requires further research. Nevertheless, this mechanism is capable of providing a consistent explanation for the rise of strength and toughness of particulate composite, at least phenomenally. Hence it must be fundamental for the improvement of toughness in ceramics toughened by dispersion, as is the mechanism of crack deflection which is to follow.

4.2 Crack Deflection

In this mechanism, various discrepancies in property existing between constituent phases produce deflections of the main crack around dispersed particles, thereby contributing to the improvement of toughness of the



- (1) (a) 主クラック面の傾き
 (2) (b) 主クラック前縁のねじれ

Figure 4. Diagram of Crack Deflection

Key:

1. Deflection of the main-crack plane
2. Twisting of the front edge of a main crack
3. Original front edge of a main crack

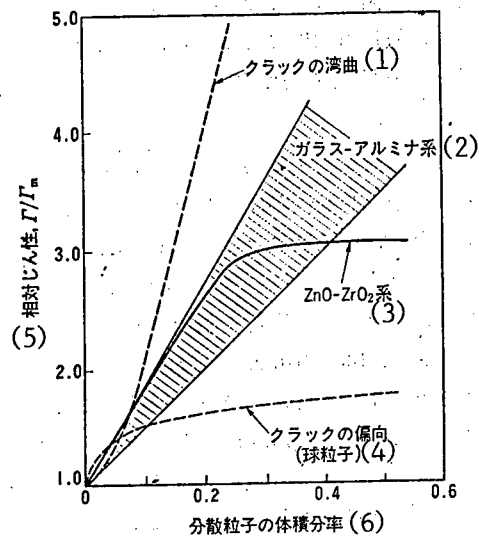


Figure 5. Comparison of the Rise of the Level of Toughness Between a ZnO Matrix-ZrO₂ Particle Composite¹⁵⁾ and Glass-Spherical Alumina Particle Composites¹⁶⁾

Key:

1. Crack bowing
2. Glass-alumina type of composites
3. ZnO-ZrO₂ type of composites
4. Crack deflection (spherical particles)
5. Relative toughness
6. Ratio in volume of the dispersed particles

material. Whereas the crack bowing described in section 4.1 refers to the change of the front edge of a crack from linear to non-linear form, the crack deflection is a change of the crack plain from planar to non-planar form. Figure 4 shows the deflection of cracks diagrammatically: in (a) an advancing crack is bent by a particle and produces a deflected plane. In cases where such crack deflections take place at adjacent particles in a direction of deflection converse to one another, the crack front will be distorted as shown in (b)--the direction of the advance of the crack in (b) is perpendicular to the plane of the paper. Farber,¹⁴⁾ et al., theoretically analysed this mechanism and concluded that the rise in toughness in this mechanism is not dependent on the size of dispersed particles but only on the ratio in volume and the shape of the particles. In terms of shape, particles of rod form and hence of high aspect ratio are the most efficient in producing deflection and, according to their computation, particles with an aspect ratio of 12 result in a fracture energy four times as large. Spherical particles dispersed in ceramics, in turn, contribute only in a limited measure to the rise of toughness of the material by this crack-deflection and energy-dissipation mechanism.

Though crack deflection may be a basic mechanism involved in a composite material wherein discrepancies exist in properties between the matrix and the dispersed particles, it is generally thought to occur together with the crack bowing described in section 4.1. It is hard, in the present stage of development, to estimate the contributions of these two mechanisms quantitatively and separately. Figure 5 represents a plot of the toughness of materials versus the fractional volume of dispersed particles for a composite material of zink oxide matrix and zirconia particles¹⁵⁾ and also for four groups of composite materials of glass matrix and alumina spherical particles examined by Swearengen, et al.¹⁶⁾

In the ZnO-ZrO₂ series above, the cubic ZrO₂ particles have all been subjected to phase transition to the monolinic ZrO₂ during the process of cooling in the manufacture of the material. Microcracks, nevertheless, have not been produced because the diameters of the particles are smaller than the critical one for the microcrack development. Moreover, measurement of acoustic emission (AE) in the course of a bending test on a test specimen detected no AE signals until just prior to the time of fracture suggesting that microcracking mechanism to be described below has not worked here. The glass alumina composite above examined by Swearengen, et al., in turn, has 25-micron spherical alumina particles dispersed in itself with only slight discrepancy in thermal expansion coefficient involved between the two phases (the difference in thermal expansion coefficient between the matrix and the particle: $\alpha_m - \alpha_p = +2.7 \times 10^{-6} \text{ K}^{-1} \sim -3.7 \times 10^{-6} \text{ K}^{-1}$) and, hence, makes a system wherein microcracking mechanism contributes only negligibly to fracture. The two broken curves in the figure represent theoretically predicted values of the toughness of this ceramic involving spherical particles which is increased by virtue of either crack-bowing or crack-deflection mechanism (calculated by Ruf, et al.¹⁵⁾). Relevant experimental values are located between these two curves, suggesting that the crack deflection and the crack bowing are involved as the major mechanisms for improving the toughness of these composite materials. Miyata, et al.,¹³⁾ took measurements of fracture toughness and acoustic emission on a glass-alumina

composite wherein spherical alumina particles of diameter 50 microns are dispersed in glass ($\alpha_m - \alpha_p = 2.8 \times 10^{-6} \text{ K}^{-1}$) and reported that the behavior of fracture toughness coincided with the one obtained by Swearengen, et al., and that, for spherical-alumina-particles-dispersed in glass involving a discrepancy in the thermal expansion coefficient of the order given above, the microcracking contributes only negligibly to the improvement of the toughness of the material.

Faber, et al., meanwhile, produced cracks by means of an indentation method in the crystalline glass $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ of two types different in heat treatment, observed the paths of the crack produced by means of the scanning electron microscope, and worked out a cumulative frequency distribution of the deflection angles as shown in Figure 6. Observation by the microscope revealed that the crystal particles $\text{Li}_2\text{Si}_2\text{O}_5$ in these crystalline glasses were in rod form with an aspect ratio R of over 12. It is conceivable that, in composite materials with such rod particles of a high aspect ratio dispersed therein, the contribution of the crack bowing mechanism to the toughness of the material is relatively poor, whereas that of the crack deflection predominates. The increase in toughness of these crystalline glasses, that is, $T/T_m \approx 3$, meanwhile, is considerably lower than the value theoretically predicted on the assumption of an aspect ratio R of 12. Observations of the paths of cracks, in this connection, revealed that the $\text{Li}_2\text{Si}_2\text{O}_5$ particles were not necessarily bypassed by the crack but often destroyed by them and hence the actual aspect ratio is $1 < R < 5$. This is consistent with the fact that, in Figure 6, the cumulative frequency distribution of the deflection angles does not agree with the theoretical curve with an assumed R of 12 but nearly with the one of R 3 or 4. It is evident that the destruction of dispersed particles reduces the effect of crack deflection. A similar analysis has been conducted in connection with the fracture analysis of the crystalline glass cordierite.¹⁶⁾

4.3 Microcracking

This mechanism of toughening ceramics involves a development and growth of microcracks in a non-linear elastic region, the so-called process zone, in the vicinity of advancing crack front; these microcracks reduce the modulus of elasticity in the region, thereby diminishing the intensity of stresses in the vicinity of the main-crack front, which is equivalent to shielding the main-crack front from external stresses of loading. The causative factors for the development and growth of microcracks are discrepancies between the properties of the matrix and the second-phase particles and, in particular, that of thermal expansion coefficient.

Improvement of the toughness of a ceramic by the mechanism of microcracking is dictated largely by the size, the shape, and ratio in volume of the dispersed particles. It has been revealed experimentally that dispersed particles are most effective when their sizes are close to a limiting particle diameter at which thermal stress due to the difference in thermal expansion coefficient of the constituent phases is the exclusive factor for producing microcracks¹⁹⁾⁻²²⁾ and that the dispersion of particles of edgy forms which are more apt to produce microcracks than for a round form, seems to be the more effective.^{13),22)} Claussen, et al.,^{19),20)} produced, by hot pressing,

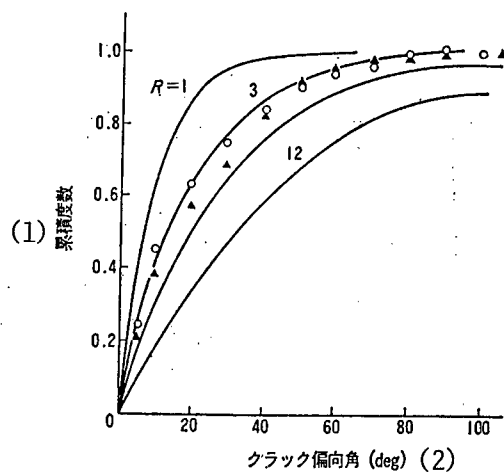


Figure 6. Cumulative Frequency Distribution of the Angle of Crack Deflections in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ Group of Crystalline Glass¹⁷⁾ Together with Relevant Theoretical Curves Based on the Assumption of Some Aspect Ratios for the Rod-Form Particles

Key:

1. Cumulative frequency
2. Angle of crack-deflections

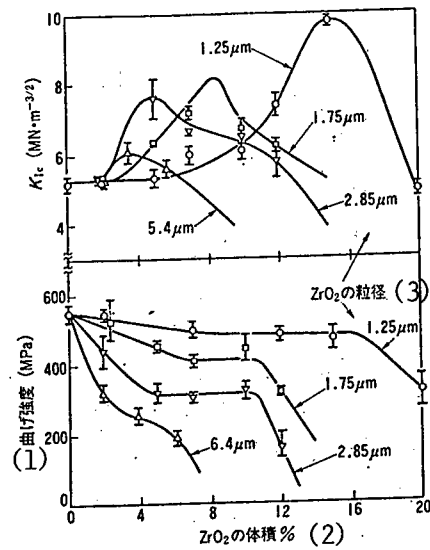
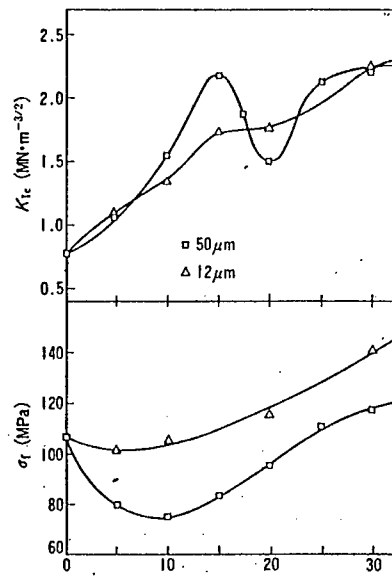


Figure 7. Fracture Toughness and Bending Strength for an Al_2O_3 Matrix- ZrO_2 Particle Composite

Key:

1. Bending strength
2. Percent in volume of ZrO_2
3. Particle diameter of ZrO_2



Percent in volume of alumina particles

Figure 8. Fracture Toughness and Strength of a Glass-Alumina Composite in Which Alumina Particle of Edgy Shapes Are Dispersed¹³⁾

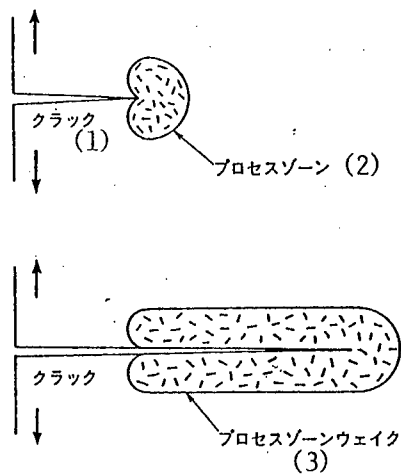


Figure 9. Process Zone and Process-Zone Wake

Key:

1. Crack
2. Process zone
3. Process-zone wake

composite materials in which non-stabilized zirconia particles of various diameters are dispersed in the alumina matrix, and examined their fracture toughness and bending strength.

The result, shown in Figure 7, revealed that the addition of the zirconia produced some lowering in bending strength but doubled the fracture toughness, K_{Ic} , at the maximum and that, as the particle diameter decreases, the K_{Ic} tends to rise and the bending strength to go down less. In these composite materials, the test specimens have undergone a volume expansion because of its phase transition from the hexagonal to the monoclinic system during the cooling process of its manufacture, thereby producing numerous cracks. The increase in the K_{Ic} has been accounted for by Claussen, et al., as due to the development and growth of microcracks in the process zone which act to dissipate the fracture energy.

As can be seen from the figure, the K_{Ic} displays a distinct maximum, suggesting that the crack density in the process zone reaches its critical value and the effect of crack connection grows. In Figure 8 are presented plots of fracture toughness and bending strength for a glass-alumina particle composite in which alumina particles of edge shape with diameters of 12 microns and 50 microns are dispersed in a glass matrix whose thermal expansion coefficient is larger than that of the particles.¹³⁾ ($\alpha_m - \alpha_p = 5.0 \times 10^{-6} \text{ K}^{-1}$) The composite system with alumina particles of 50 microns dispersed therein was found to have developed numerous microcracks in the process of cooling during the manufacture of its test specimens whereas the one with the particle of 12 microns was not. In the process of the bending test on specimens of these systems, AE signals were detected before the fracture load was reached and, in the case of the composite involving 12-micron particles, even at comparatively low loads. In both systems, the microcracking seems to work in the fracture process as a major mechanism for the dissipation of fracture energy.

A number of approaches have been made to the improvement of the toughness of ceramics by the microcracking mechanism. ^{21),23),24)} the condition in which this mechanism works effectively while the fall of the strength of the material involved is limited to the minimum, however, has not yet been elucidated as has also been the possible level to which the toughness of the ceramic is raised. Evans, et al.,²⁴⁾ have recently postulated a mechanical model by which to understand the rise of toughness produced by microcracking mechanism and discussed the cause of the rise of the toughness of materials and levels of relevant rises. As shown in Figure 9, the (frontal) process zone arising in front of the advancing edge of the main crack is converted into the process zone wake located along the surface of the crack as the crack extends. They made a theoretical analysis of the effect of the frontal process zone and the process zone wake for shielding the stress involved at the front edge of the main crack.

Even though the development and growth of microcracks in the frontal process zone causes reduction of the modulus of elasticity in that zone, the very microcracks developed also produce a concomitant fall of the toughness there, which, in turn, acts adversely to the fall of the modulus of elasticity above and, consequently, to the effect of shielding the stress. There is no

possibility, therefore, of a substantial rise in the toughness of materials as far as the frontal process zone in front of the maincrack edge is concerned. Evans, et al., concluded that the residual-strain energy built up in the process zone wake, rather, exerts the major effect in shielding the stress at the front of the main crack. The source of the residual energy, in turn, is a permanent strain or an expansion in volume due to the microcracks produced by the action of residual tensile stress and keeping open in the process zone wake. This expansion in volume, to be brief, suppresses the main crack and reduces the stress at the front of the main crack conceivably. The above effect in the process zone wake is represented by the R curve effect²⁵⁾ in the values of toughness estimated and, if the effect is sufficiently large, has to be dealt with as a non-linear fracture phenomenon.

5. Conclusion

Besides the three major mechanism of dissipating the fracture energy described above, branching of cracks, blunting of the edge of a crack, and bridging of fractured surfaces are among the general mechanisms involved, whereas stress-induced phase transition in the system involving dispersed zirconia particles is of importance as a special one. It is important that these mechanisms involved in fracture work not singly but in combination and not independently but in close association with each other. The extent to which and the manner in which an individual mechanism contributes to the rise of toughness of a material, therefore, varies with the nature of the other mechanisms which work simultaneously. Since not only has each mechanism for dissipating fracture energy been elucidated sufficiently but also most of the theoretical approaches are based on the assumption that a single mechanism for the dissipation of fracture energy works in the fracture process, it is often difficult to isolate and quantitatively estimate the individual contribution of each mechanism to the improvement of toughness of a ceramic from relevant data experimentally prepared.

The theories on the mechanisms of raising the toughness of ceramics described above involve many assumptions and approximations; experimental data for verifying their consistency, nevertheless, have not been sufficiently available. It is hoped that building up of relevant data be pushed ahead in the coming years.

FOOTNOTES

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Toughening Ceramic Materials by Zirconia

Tokyo CERAMICS JAPAN in Japanese Jul 86 pp 613-619

[Article by Tsugio Sato and Masahiko Shimada, Faculty of Engineering, Tohoku University]

[Text] 1. Introduction

With excellent resistance to heat, strength at high temperature, resistance to creep, resistance to corrosion, and resistance to abrasion and with relatively low density, ceramics are superior to metal and organic polymer raw materials in many properties needed in structural materials. Hence they have the prospect of being put to use in structural materials that have to undergo harsh operating conditions which metal and organic polymer materials are unable to withstand, for example, in high-efficiency thermal engines, precision machine parts, bioadaptable materials and other like products in new industrial sectors, with their practical application having been accomplished

in parts of the engine parts, tooth materials, seal materials, etc. In spite of their high strength comparable to metallic materials even at room temperature, ceramics, however, are poor in toughness, brittle, and easy to fracture and, hence, not sufficiently safe and reliable, posing a major problem in their practical application. Much research, therefore, has been promoted with the view to improving their strength and toughness and thereby substantiating their reliability.

The basis of estimating and improving the strength and toughness of ceramics is given by the formula

$$K_{Ic} = (2 E \gamma_i)^{1/2} = \sigma_f Y \sqrt{c} \quad (1)$$

where K_{Ic} denotes critical stress intensity factor, σ_f fracture strength, c length of cracks, E Young's modulus, γ_i fracture energy, and Y crack shape factor. It is evident from the above formula that the development of ceramics of high toughness requires an improvement in Young's modulus and the fracture energy. Whereas Young's modulus is a value inherent to a ceramic, the fracture energy is improved notably by the formation of composite materials involving a second component and, hence, developmental research was initially pushed ahead on composite materials wherein metals, second-phase ceramics, ceramic fibers, whiskers, etc. were dispersed in a ceramic. These composite materials have a higher fracture energy and higher toughness because of the development of compressive stress and microcracks resulting from a difference in the coefficient of thermal expansion, crack bowing from the pinning by dispersed particles, and pull out of fibers, among other things.

Gravice, et al., meanwhile, reported in 1975 in an article on "Ceramic Steel?" that an enormously high value of toughness was exhibited by a part-stabilized zirconia (PSZ) produced by keeping zirconia, ZrO_2 , of the tetragonal system, which is stable at high temperature, in semistable state at room temperature. The new mechanism of toughening referred to as transformation toughening involves, at the crack front a martensite type of transformation of zirconia from the tetragonal system to the monoclinic system, which is stable at low temperature. This transformation, in turn, acts to dampen the fracture stress and hence afford a high strength and toughness to the ceramic. Since the discovery of PSZ, much research has been conducted on ceramic materials toughened by the composite formation with zirconia, leading to, for example, a composite material, $Al_2O_3-ZrO_2(Y_2O_3)$ with a bending strength of 2,000-2,500 MPa, and a fracture toughness of 6-8 $MPa \cdot m^{1/2}$ --a strength and a toughness far surpassing those for conventional ceramic materials.

2. Microscopic Structure of Zirconia Ceramics of High Strength and Toughness

Typical zirconia ceramics of high strength and high toughness include those involving CaO, MgO, Y_2O_3 , or CeO_2 as a solid solution to sustain t(tetragonal) ZrO_2 . Though any of these zirconia ceramics is capable of dampening the fracture energy by virtue of the $t \rightarrow m$ transformation, their microscopic structures differ substantially from each other. Claussen³⁾ classified the microscopic structure of zirconia ceramics involving sustained t- ZrO_2 into four types as in Figure 1. Diagram I of the figure represents the microscopic structure of the ceramic generally referred to as partially stabilized zirconia (PSZ). After the addition of a stabilizer, the zirconia is sintered at a temperature of 1,650-1,850 degrees C, the stable zone for the cubic system of zirconia, c- ZrO_2 , yielding a sintered compact of grain diameter around 50-100 microns; the compact was further subjected to heat at a temperature of 1,100-1,500 degrees C, the stable zone of t- ZrO_2 , for annealing such that fine t- ZrO_2 twines of size 0.2 micron are crystallized out in the c- ZrO_2 matrix. MgO- ZrO_2 and CaO- ZrO_2 wherein 8-10 mol percent MgO and CaO, respectively, are mixed with ZrO_2 as solid solution come under this type.

Because of the large grain diameters, this type of zirconia has fracture strength of no more than 800 MPa but a high toughness of around $12-14 \text{ MPa}\cdot\text{m}^{1/2}$ by virtue of a large $t \rightarrow m$ transformation layers. Diagram II shows a zirconia compact which is prepared by sintering a solid solution of zirconia and either 2-4 mol percent Y_2O_3 or 9-14 mol percent CeO_2 at a temperature of 1,350-1,600 degrees C, the stable zone for t- ZrO_2 , such that the grain diameter be controlled in the range of 0.3 to 2.0 microns. The constituent grains are largely made up of t- ZrO_2 and referred to as the tetragonal zirconia polycrystals, TZP. The constituent particles of the TZP, made up almost exclusively of t- ZrO_2 which is capable of $t \rightarrow m$ transformation, exhibit a high value of toughness.

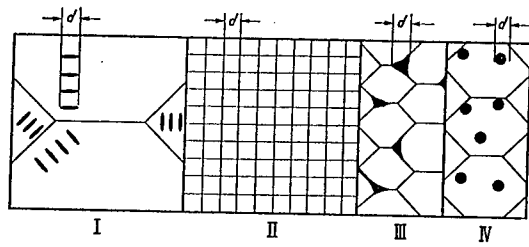
The TZP also involves fewer defects because the particle is very fine and exhibits strength of 1,000 to 1,500 MPa.⁴⁾ Diagrams III and IV show the dispersion toughened type of ZrO_2 ceramics. The former is the most common ZrO_2 -reinforced ceramic in which either PSZ or TZP grains are dispersed and mingled with some ceramic particles, whereas, in the latter, either PSZ or TZP is crystallized out inside some other ceramic particles as seen in cases where Al_2O_3 and ZrO_2 are fully blended and sintered.⁵⁾

Though the IV types of ceramics sustains t- ZrO_2 of larger grain diameters than does the III type, the toughening effect due to transformation in that type is possible only in cases where the fracture in the grains takes place.

3. Mechanism of Toughening of Zirconia Ceramics

3.1 Toughening by Means of Stress-Induced Transformation

Since the toughening by means of stress-induced transformation results from the transformation from t- ZrO_2 to m- ZrO_2 occurring at the edge of cracks which, in turn, acts to dampen the fracture stress applied (Figure 2(a)), it is essential that the t- ZrO_2 be kept at room temperatures and its design needs thermodynamic and dynamic considerations.

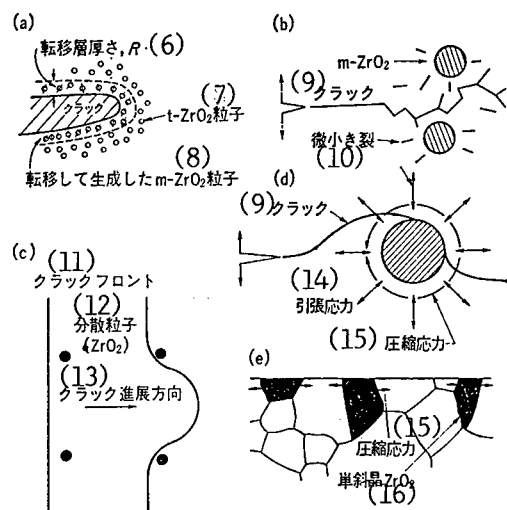


- (1) I : 部分安定化ジルコニア ($d \approx 0.2 \mu\text{m}$)
 (2) II : 正方晶ジルコニア多結晶体 ($d \approx 0.2 \sim 2 \mu\text{m}$)
 (3) III : 粒界分散ジルコニア ($d \approx 0.5 \sim 10 \mu\text{m}$)
 (4) IV : 粒内分散ジルコニア ($d \approx 0.2 \sim 1 \mu\text{m}$)

Figure 1. Diagrams of the Typical Microscopic Structures of Zirconia Ceramics³⁾

Key:

1. Partially stabilized zirconia
2. Tetragonal zirconia polycrystals
3. Zirconia dispersed in the grain boundary
4. Zirconia dispersed in the grain



- (1) (a) 応力誘起相転移 (b) 微小き裂によるき裂分岐 (2)
 (3) (c) き裂の湾曲 (d) き裂の曲げ (4)
 (5) (e) 表面圧縮応力

Figure 2. Mechanism of Toughening of Zirconia Ceramics

Key:

1. Stress induced transformation
2. Branching of cracks due to micro-cracks
3. Crack bowing
4. Crack deflection
5. Compressive stress over the surface
6. Thickness of the transformation layer, R
7. t-ZrO₂ particles
8. m-ZrO₂ particles produced by the transformation
9. Crack
10. Micro-cracks
11. Crack front
12. Dispersed particle
13. Direction of advance of the crack
14. Tensile stress
15. Compressive stress
16. Monoclinic ZrO₂

Allowing for chemical-free-energy change ΔG_c , strain energy change ΔG_{se} , and surface energy change ΔG_s as the energy change involved in the $t \rightarrow m$ transformation, Lange has made theoretical discussion on $t\text{-ZrO}_2$ for its stability and for its toughening resulting from the transformation.⁶⁾

$$\begin{aligned}\Delta G_{t \rightarrow m} &= (G_c^m - G_c^t) + (G_{se}^m - G_{se}^t) \\ &\quad + (G_s^m - G_s^t) \\ &= -|\Delta G_c| + \Delta G_{se} + \Delta G_s\end{aligned}\quad (2)$$

ΔG_c is represented as $-|\Delta G_c|$ in the above formula by Lange because ΔG_c has negative values in the low temperature zone where the $t \rightarrow m$ transformation takes place. Figure 37) represents the phase diagram of the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system. It is evident from the figure that ΔG_c increases or $|\Delta G_c|$ decreases with the amount of the stabilizer constituent of the solid solution and with temperature. The ΔG_{se} , in turn, is given by

$$\Delta G_{se} = \frac{E_c}{6} (\Delta V/V)^2 \quad (3)$$

The value is positive since the transformation involves expansion in volume of around 4 percent and increases with an increase of Young's modulus. The ΔG_{se} is partly dampened in cases where formation of microcracks and twines accompanies the transformation. The ΔG_s in the formula represents the sum of the increase of the surface areas of the particles due to the transformation and that of the microcracks and twines formed, which are both positive. Lange estimates that the value is inversely proportional to the diameter of the grain according to the formula

$$\begin{aligned}\Delta G_s &= 6(r_m - g_s r_t)/D + 6r_c g_c/D + 6r_t g_t/D \\ &= 6 \sum r_g/D\end{aligned}\quad (4)$$

and that change in surface energy due to crack formation is 10 times that for grains and change in surface energy due to twin formation equivalent to that for grains.

The estimation of the change of values ΔG_{se} and ΔG_s above resulting from the formation of microcracks and twines are not based on either theoretical or an experimental base and formulas (2)-(4), hence, do not allow to draw an accurate equilibrium phase diagram. Nevertheless, it affords information on the stability of $t\text{-ZrO}_2$ semiquantitatively, that is, in order to keep $t\text{-ZrO}_2$ stably at room temperatures, it is evident that the stabilizer constituent of the solid solution will be increased, Young's modulus will be improved, and the diameter of the grains will be diminished.

Where fracture toughness afforded by the $t \rightarrow m$ transformation is concerned, Lange obtained the following formula (5) and McMeeking, et al.,⁸⁾ the formula (6):

$$K_c = [K_0^2 + 2(|\Delta G_c| - \Delta G_{se} f) \frac{E_c V_i R}{(1 - \nu_c^2)}]^{1/2} \quad (5)$$

$$K_c = K_0 + \eta V_i \Delta V E_c \sqrt{R/(1 - \nu_c)} \quad (6)$$

Where K_0 denotes the fracture toughness of the matrix, R the thickness of the transformation layer, V_i the volume fraction of $t\text{-ZrO}_2$, ν Poisson's ratio, η a

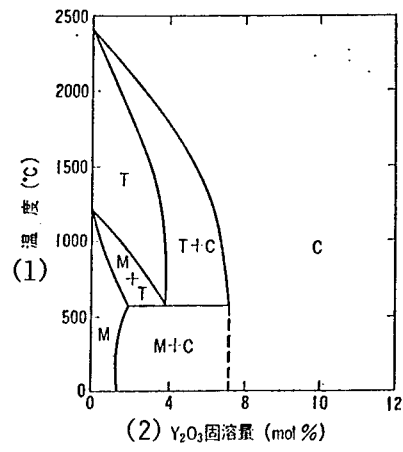


Figure 3. Phase Diagram of $\text{ZrO}_2\text{-Y}_2\text{O}_3$

Key:

1. Temperature
2. Quantity of Y_2O_3 in the solid solution

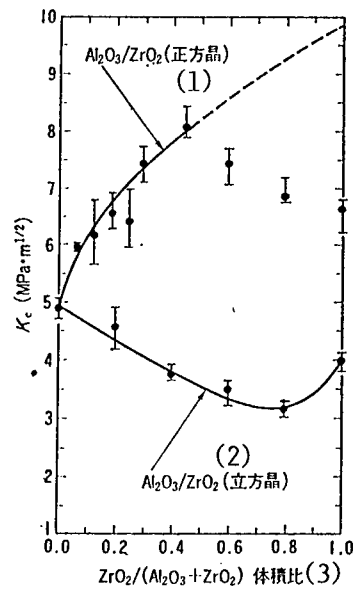


Figure 4. Fracture Toughness of the Composite $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$

Key:

1. Tetragonal system
2. Cubic system
3. Ratio in volume

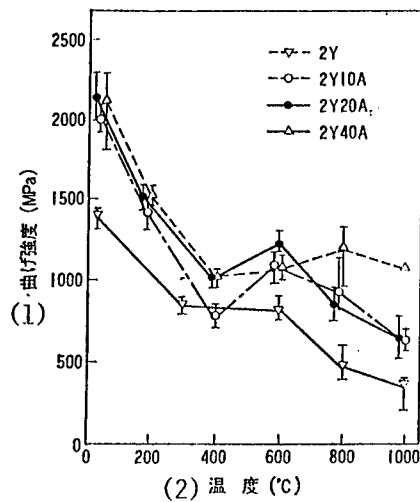


Figure 5. Dependence on Temperature of the Fracture Strength of the Composite ZrO_2 (2 mol percent Y_2O_3) Al_2O_3

Key:

1. Bending strength
2. Temperature

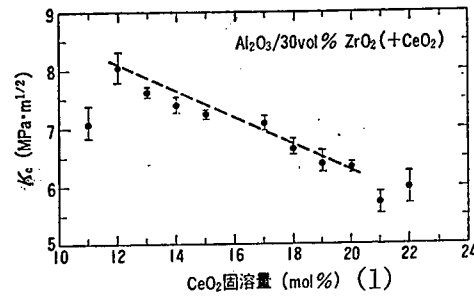


Figure 6. Plot of the Quantity of CeO_2 in the Solid Solution Against the Fracture Toughness of the $\text{ZrO}_2(\text{CeO}_2)\text{-Al}_2\text{O}_3$ Composite

Key:

1. Quantity of CeO_2 in the solid solution

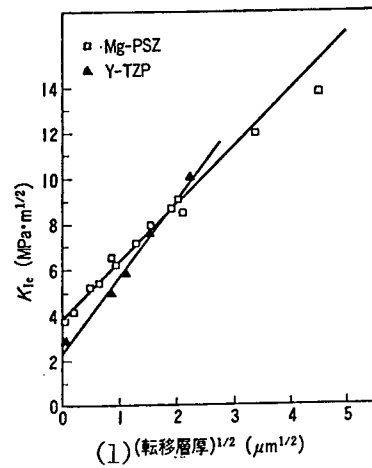


Figure 7. Plot of the Fracture Toughness of Mg-PSZ and Y-TZP Against the Thickness of the Transformation Layer⁹⁾

Key:

1. Thickness of the transformation layer

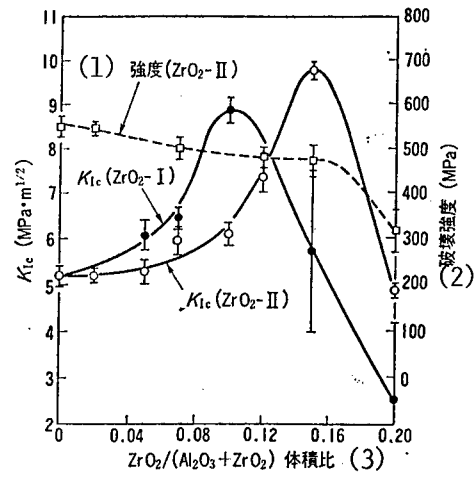


Figure 8. Fracture Strength and Fracture Toughness of the Composite $\text{Al}_2\text{O}_3\text{-ZrO}_2$

Key:

1. Strength
2. Fracture
3. Ratio in volume

constant, ΔV volume expansion rate, and f the rate of the release of the strain energy by virtue of microcracking and twine formation.

Figure 4 represents a plot of the fracture toughness of the composite material $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$:⁶⁾ The dispersion of c-ZrO₂ in Al_2O_3 produces no notable change in the relevant property, whereas that of t-ZrO₂ resulted in a change of the value from 5 $\text{MPa}\cdot\text{m}^{1/2}$ to 10 $\text{MPa}\cdot\text{m}^{1/2}$ as the proportion of t-ZrO₂ or V_1 increases. The fall of toughness at V_1 over 0.5 may conceivably be due to that of Young's modulus among other things. Figures 5 and 6, in turn, indicate that dispersion of Al_2O_3 leads to an increase in Young's modulus and hence to an increase of strength at high temperatures and that both ΔG_c and toughness drop as the volume of CeO_2 in solid solution increases. Swain has made measurement of Mg-PSZ and Y-PSZ of different grain diameters and proved that the thickness R of the transformation layer increases and toughness of the materials improves with increasing grain diameter as shown in Figure 7; these empirical values are in agreement with values predicted by formulas (5) and (6).

3.2 Toughening of Ceramics by Means of Microcracking

It is been well known that branching of cracks (Figure 2(b)) due to microcrackings produced by a difference in thermal expansion coefficient between the matrix and the dispersed particles is effective as a means of toughening of ceramics.¹⁰⁾ The tensile strength arising in the matrix around a spherical grain when the temperatures falls from T_0 to T_1 is given by the formula

$$\sigma_t = (\alpha_m - \alpha_p)(T_1 - T_0)(R/r)^3 / 2[(1 + \nu_m)/2 E_m + (1 - 2\nu_p)/E_p] \quad (7)$$

Where α_m stands for the thermal expansion coefficient of the matrix, ν_m the Poisson's ratio of the matrix, α_p the thermal expansion coefficient of the dispersed particles, ν_p the Poisson's ratio of the dispersed particles, R the radius of the dispersed particles, and r distance from the center of the particle.

Particles with a diameter greater than the critical grain diameter D_c given by

$$D_c \geq k/\sigma_t^2 \quad (8)$$

need to be dispersed if microcracks are to be formed.¹⁰⁾

The difference in thermal expansion coefficient between commonly available ceramics is not very large, which makes it necessary that the value D_c be large. In cases where sufficiently large particles produce microcracks, cracks are apt to be larger than the critical length of fracture c , thereby reducing strength though toughness is improved. In contrast, the t \rightarrow m transformation of ZrO₂, involving as large as 4 percent expansion in volume, is capable of producing microcracks even if the particles are very small and thus achieving improvement in the toughness of the material without lowering of strength. In Figure 8, fracture strength and toughness are examined for sintered compacts of ZrO₂ of 3 to 5 microns dispersed in Al_2O_3 in which

microcracks are produced by means of $t \rightarrow m$ transformation in the cooling process.¹¹⁾ At ZrO_2 10 to 15 percent in volume, the K_{Ic} of the compact jumped to $9 \sim 10 \text{ MPa}\cdot\text{m}^{1/2}$ or around double that of the compact involving Al_2O_3 alone, while the bending strength remained almost stationary. Further increase of the proportion of ZrO_2 , nevertheless, led to notable fall in toughness because the microcracks merged with each other and turned into larger ones.

3.3 Toughening of Ceramics by Virtue of Crack Bowing and Crack Deflection

Pinning of the front of a crack by particles produces a bowing of the front as shown in Figure 2(c).¹²⁾ Compressive stress in the matrix around a dispersed particle, in turn, causes deflection of the course of cracks around the particle as seen in Figure 2(d).¹³⁾ These changes both produce an increase in the fracture energy required and improvement of toughness in the material. The above $t \rightarrow m$ transformation, meanwhile, involving a volume expansion, produce a compressive stress in cases microcracks fail to develop. Ruh and Evans, with the view to elucidating the effect of compressive stress by ZrO_2 particles, prepared sintered compacts that can block the development of microcracks by dispersing $ZrO_2(Y_2O_3)$ of different Y_2O_3 contents in the matrix ZnO .¹⁴⁾ As shown in Figure 9, the fracture toughness of the compact is not governed by the amount of $t\text{-}ZrO_2$ but displayed excellent correlation with the amount of $m\text{-}ZrO_2$ added, increasing about three times that of the compact of no $m\text{-}ZrO_2$ addition.

Since the increase in the value of toughness is substantially higher than the value predicted on the basis of the crack deflection effect, the crack-bowing effect has also to be allowed for in the relevant assessment.

3.4 Improvement of Toughness Due to Surface Compressive Effect

The $t \rightarrow m$ transformation produced by the polishing, etc. of the surface of a sintered compact involving $t\text{-}ZrO_2$ leads to expansion in volume of the ZrO_2 and, hence, a surface compressive effect, which serves to improve the toughness of the compact (Figure 2 (e)). Possible means of facilitating transformation at the surface are: addition, into the surface layer, of HfO_2 , etc., which improve the critical transformation temperature, as a component of a solid solution; producing crude and large particles at the surface by such means as providing temperature distribution during sintering or concentration distribution of sintering assistants.³⁾

In addition to the above, the strength and toughness of a compact may sometimes be enhanced by means of a stepped-up compactness or suppression of the grain growth in the matrix by virtue of the dispersion of ZrO_2 particles. In many cases, however, the effects of the means described above are difficult to evaluate separately; they serve in combination to enhance the toughness of a compact. Table 1 presents the toughness and the strength at room temperature of major ceramics with ZrO_2 reinforcement reported to date. It is evident that these have higher strength and toughness than the nonreinforced compacts.

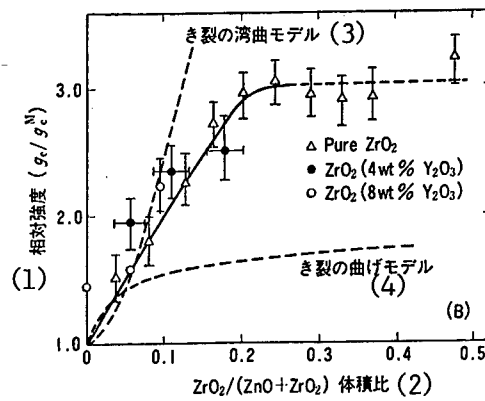


Figure 9. Fracture Toughness of the ZnO-ZrO₂ Composite

Key:

1. Relative strength
2. Ratio in volume
3. Model for the crack-bowing
4. Model for the crack deflection

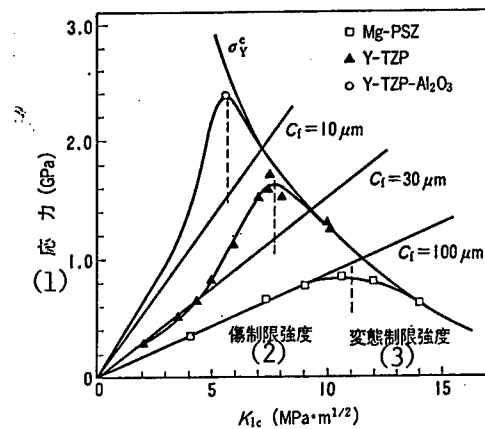


Figure 10. Strength and Fracture Toughness for the Ceramics Mg-PSZ, Y-TZP, and Y-TZP-Al₂O₃

Key:

1. Stress
2. Strength governed by cracks
3. Strength governed by transformation

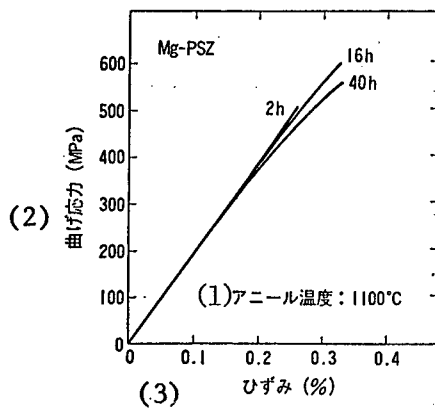


Figure 11. Plot of Bending Stress Versus Strain for Mg-PSZ's

Key:

1. Annealing temperature
2. Stress
3. Strain

Table 1. Strength and Toughness of the ZrO₂ Group of Ceramics

Ceramic Material	Matrix With No ZrO ₂ Combined		Matrix with ZrO ₂	
	K_{Ic} (MPa-m ^{1/2})	σ_f (MPa)	K_{MIc} (MPa-m ^{1/2})	σ_f (MPa)
c-ZrO ₂	2.4	180	2 ~ 3	200 ~ 300
PSZ			6 ~ 8	600 ~ 800
TZP			7 ~ 12	1,000 ~ 2,500
Al ₂ O ₃	4	500	5 ~ 8	500 ~ 1,300
Mullite	1.8	150	4 ~ 5	400 ~ 500
Spinel	2	180	4 ~ 5	350 ~ 500
Al ₂ TiO ₂	0.8	40	2.5 ~	120
Cordierite	1.4	120	3	300
Si ₂ N ₄	5	600	6 ~ 7	700 ~ 900

4. Toughness and Strength of Zirconia Ceramics

Figure 10 presents the relationships between strength and toughness for the Mg-PSZ, Y-TZP, and Y-TZP-Al₂O₃ ceramics. As can be seen from the figure, materials of high strength are of low toughness and materials of high toughness are of low strength. Namely, the proportional relationship between fracture toughness as represented by the formula (1) above does not hold true generally for ZrO₂ ceramics. Figure 11 represents a plot of stress versus strain for Mg-PSZ's of different t-ZrO₂ grain diameters, which is annealed for 2, 16, and 40 hours at 1,100 degrees C.⁹⁾ The toughness of the compacts increases with increasing t-ZrO₂ grain diameter and is largest for the compact annealed for 40 hours though the strength is largest for the one annealed for 16 hours. It can be seen from the figure that the specimen annealed for 2 hours exhibits elastic behavior whereas non-elastic behavior is increasingly notable with increasing high toughness of the specimen. This implies that ZrO₂ compacts of higher toughness has the t→m transformation brought about at a certain stress and thus cracks formed in them which, upon reaching the critical length, end up in fracture. In Figure 10, the region where the plot of σ_f versus K_{Ic} is linear as given by formula (1), cracks in the specimen govern the strength, and critical crack lengths are estimated at 100 microns and 30 microns for Mg-PSZ and Y-TZP, respectively. In the region of still higher toughness, on the other hand, the strength is dictated by transformation, that is, the strength is equivalent to the stress producing transformation. Swain made a prediction of the maximum strength or critical strength of the compacts, σ_Y^c , using the formula (6) above and the formula (9) below¹⁵⁾ which represents the relationship between toughness and tensile strength around a crack in the yield-point region and demonstrated a fine agreement between the theoretical and empirical values as represented in Figure 10.

$$\sigma_Y = \frac{K_{Ic}}{\sqrt{2\pi c}} f(\theta) \quad (9)$$

It is evident from formulas (6) and (9) that an increase in Young's modulus or the proportion of t-ZrO₂ permits an increase in toughness and critical strength. In fact, a high strength of 2,500 MPa and a high fracture toughness of 6.0 MPa-m^{1/2} was attained, as shown in Figure 10, for a composite material made up of ZrO₂-2-mol-percent Y₂O₃, the t-ZrO₂ single phase, and Al₂O₃ of high Young's modulus. In materials at the critical strength, the strength is not affected by cracks, etc., in the specimen and, hence, the material must have a high Weibull coefficient and make a raw material of high reliability, conceivably. The critical strength also represents the limiting value of toughening a material by means of transformation. Further toughening and strengthening of a material, therefore, requires the use of other relevant mechanisms in combination such as crack bowing, crack deflection, and pull out of fibers. Strengthening by means of whiskers, among other things, seems effective.

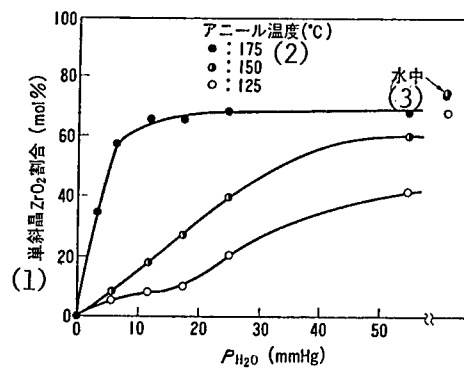


Figure 12. Transformation of Y-TZP by Means of Annealing in Humid Atmosphere

Key:

1. Ratio of monoclinic ZrO_2
2. Annealing temperature
3. In water

5. Problems in Zirconia Ceramics

The ZrO_2 ceramics have been afforded a higher toughness and strength by virtue of the new toughening mechanism of transformation. However, because of the very toughening mechanism, problems described below are posed.

5.1 Lowering of Strength at High Temperature

Since the change in chemical free energy, ΔG_c , involved in the $t \rightarrow m$ transformation increases with an increase in temperature, the toughness of the material falls with rising temperature and, at high temperatures where the tetragonal phase is the stable one, at around 800 degrees C for $\text{ZrO}_2\text{-Y}_2\text{O}_3$ for example, no strengthening of the compact is available. The upper limit of the temperature for transformation is raised by the addition of HfO_2 to ZrO_2 in the form of the solid solution, which, nevertheless, makes it difficult to keep the tetragonal system at room temperature. Formation of a composite material made of ZrO_2 and a material superior in strength at high temperature such as alumina, mullite, and non-oxide ceramics (SiC , Si_3N_4 , etc.) seems, after all, to provide methods best adapted to improving the strength at high temperature and Claussen reported SiC whiskers as promising for the relevant purpose.³⁾

5.2 Decrease in Strength Resulting From Annealing at Low Temperature

The strength of PSZ and TZP falls notably when subjected to annealing at a low temperature of around 200 degrees C because the $t\text{-ZrO}_2$ maintained under a semistable condition undergoes transformation, by the annealing into $m\text{-ZrO}_2$, the stable phase at low temperature, and thereby develops microcracks.¹⁵⁾ Transformation produced by annealing at low temperature starts with the surface of the specimen and is promoted notably in the presence of water, etc. as shown in Figure 12;^{16), 17)} it is conceivable, therefore, that the reaction of ZrO_2 with water, etc. involves cleavage of the O-Zr-O bond, thereby liberating the strain stress ΔG_{se} . The decrease in strength due to annealing at low temperature may be counteracted by the improvement of thermostability of the material $t\text{-ZrO}_2$; measures described in Section 1.3 such as an increase in the amount of the stabilizer in the solid solution, an improvement of Young's modulus, and reduction in the grain diameter values are all effective. It must be noted, however, that these methods diminish the toughness of a sintered compact as predicted from formula (5). It seems, therefore, that the best method is the control of the concentration of a stabilizer and of the diameter of the grain, on the one hand, and the formation of a composite material of ZrO_2 with a ceramic of high Young's modulus such as Al_2O_3 and SiC on the other such that the thermostability of the ceramic is improved and the fall of its strength prevented.

6. Conclusion

The authors reviewed above the mechanism of strengthening ceramics and pointed out that transformation toughening, while capable of affording high toughness to ceramics, involves a limitation in the enhancement of their strength and toughness and are confronted with such problems as fall of strength at high temperature and deterioration of strength after annealing at low temperature

as long as they are used alone. In this connection, raising the fracture energy means of the formation of composite material seems to be an effective countermeasure for the improvement of strength and toughness of the ceramics at high temperature and, in particular, formation of composite materials made of ZrO_2 and a material of high Young's modulus is effective in counteracting the deterioration of strength due to annealing at low temperature and in improving the strength and toughness at room temperatures. It seems possible, therefore, that ceramic raw materials superior in safety and reliability may be afforded if multi-phase composite ceramics involving ZrO_2 , materials of high Young's modulus such as Al_2O_3 and non-oxides, whiskers, etc. are explored.

FOOTNOTES

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Toughening of Ceramics by Whiskers

Tokyo CERAMICS JAPAN in Japanese Jul 86 pp 621-629

[Article by Shigeo Inoue, Tetsuo Uchiyama, both members of the Research and Development Division of the Riken Co. and Koichi Nihara, a member of the Physics Department of the National Defense Academy]

[Text] 1. Introduction

Formation of a composite material involving whiskers, as the second phase, with the view to providing a product with a higher strength than that of the original single-phase matrix is referred to as fiber reinforcement¹⁾ in the sectors of metals and plastics (FRP, FRM). This fiber reinforcement is aimed at the so-called load transfer or having the whiskers bear part of the load applied so that a notably high elasticity of the material be made the best of. If the load transfer is to be effective, the following three conditions must be fulfilled:

Condition I--Whiskers shall be dispersed uniformly in the matrix.

Condition II--The force bonding the matrix and the whisker at the interface shall be large enough to ensure the load transfer.

Condition III--Fracture elongation of the matrix shall be larger than for the whiskers.

Condition I concerns the method of manufacture and it is important that the method of dispersion best adapted to individual cases be developed. Condition II implies that in cases where bonding at the interface is poor, the load is borne not by whiskers but by the matrix alone and thus the effect of the load-transfer effect is minimized. Condition III, in turn, implies that the load-transfer effect is substantial if the fracture elongation of the matrix is larger than for the whisker and the effect is poor when the elongation of the matrix is smaller than for the whisker as shown in Figure 1.

The above conditions, except the Condition I involving methods of manufacture, are comparatively easy to meet so far as FRP and FRM are concerned: In FRPs and FRMs that involve ceramic whiskers which are the most elastic of all whiskers as seen in those of SiC and Si₃N₄, the matrix and the whiskers undergo thermal contraction upon cooling of the composite from the processing temperature to room temperature and the difference in the degree of contraction, which is greater for plastics and metals than for the whisker, produces an internal stress at the interface between the two phases, which

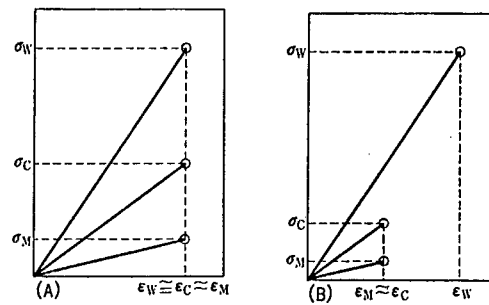


図1 ウィスカー (W), マトリックス (M),
複合体 (C) の破断伸び ($\epsilon_W, \epsilon_M, \epsilon_C$)
と破断強度 ($\sigma_W, \sigma_M, \sigma_C$) との関係
(1) (A) $\epsilon_W \approx \epsilon_M$ の場合, ウィスカーによる荷重
転移効果は大
(2) (B) $\epsilon_W > \epsilon_M$ の場合, ウィスカーによる荷重
転移効果は小²⁾

Figure 1. Elongation at Fracture ($\epsilon_W, \epsilon_M, \epsilon_C$) and Strength at Fracture ($\sigma_W, \sigma_M, \sigma_C$) for Whisker W, Matrix M, and Composite C

Key:

1. Where $\epsilon_W \approx \epsilon_M$, the effect of the transfer of load by virtue of whisker is large
2. Where $\epsilon_W > \epsilon_M$, the effect is small²⁾

acts to bond them. The fracture elongation of metals and plastics, meanwhile, far surpasses that of ceramic whiskers in general and, hence, these composite materials make couples which make the most of the load-transfer effect.

In the case of FRCs where a ceramic is coupled with a ceramic whisker to make a composite, in contrast, crack deflection, and whisker pull-out for toughening of a compact count more than does the load-transfer effect above for strengthening it. In the crack deflection, the front of the crack shuns the whisker and advances through the interface between the matrix and whisker, producing a zig-zag pattern of the crack course; this, in consequence, makes the fracture energy of the compact greater.³⁾ The whisker pull-out, in turn, involves weakening of the bond between the matrix and the whisker at the interface and subsequent pulling-out of the whisker from the matrix due to a stress concentration in the process zone in the vicinity of the crack front; this also makes the fracture energy larger in a great measure.^{4),5)} The above two mechanisms, of which the latter seems to play the dominant role in FRC, work effectively in toughening a compact under the following condition:

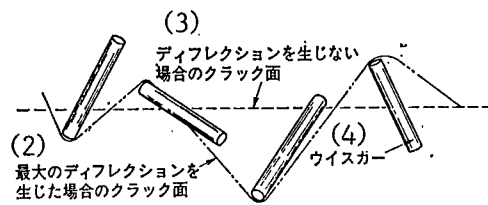
Condition IV--The force of bonding at the interface between the matrix and the whisker shall be appropriate enough to ensure crack deflection and whisker pull-out in the field of stress at the crackfront.

It is not possible for FRCs to be made tougher simply by intensifying the force of bonding at the interface as it is with FRPs and FRMs. This implies that the toughening of materials by means of whiskers comes under two categories: One is strengthening by virtue of the load-transfer effect in the absence of cracks and the other toughening by virtue of the crack deflection and the whisker pull-out in the presence of cracks. The control of the bonding force at the interface, needless to say, is the most important factor if both the strengthening and toughening of a material are to be satisfied at the same time.

2. Basic Concept for Toughening of Materials by Means of Whiskers

2.1 Mechanism of Toughening by Whiskers

The effect of the transfer of loads to whisker is the same for FRCs as it is with FRPs and FRMs. The mechanism for the toughening of materials follows: the crack deflection effect in the first place, is produced by the dispersion of a second phase in the matrix, in general, as in Figure 2. Faber, et al.,³⁾ in turn, computed the increase of fracture toughness, K_{Ic} , due to crack deflection produced by the second-phase particles as in Figure 3: The computation is based on the assumption that the interface between the matrix and the whiskers involves firm mechanical bondage. As can be seen from the figure, the K_{Ic} grows with increasing aspect ratio, that is, with the changes of the shape of the second-phase particles from sphere to disk and to rod. This implies that, providing their Young's modulus are the same, the whisker shape of a second phase is more effective than the spherical phase in producing the crack deflection and toughness. The mechanism involved is that the degree of the deflection of a crackfront, which consumes the largest energy in the crack deflection process, becomes maximal when the particles are in whisker shape.⁶⁾ Whiskers, therefore, are very effective in enhancing the

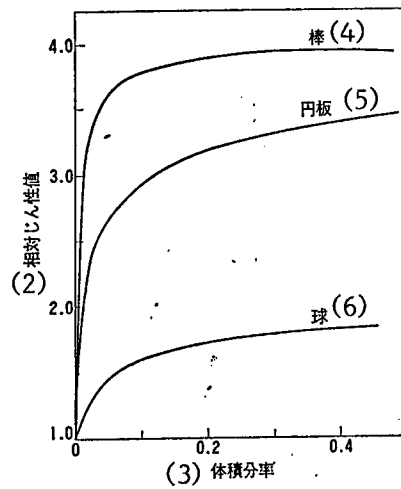


(1) アスペクト比が大になるほど、ディフレクト面のねじれの度合は大きくなる。

Figure 2. Diagram of the Crack Deflection by Virtue of Whiskers

Key:

1. The degree of deflection increases with increasing aspect ratio.
2. The [direction of the] plane of the crack when the deflection is maximal.
3. The [direction of the] plane of the crack when the deflection is zero.
4. Whisker

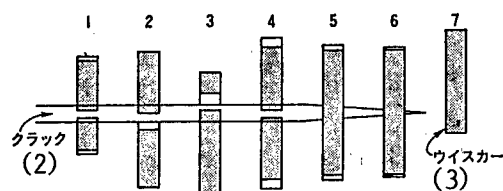


(1) 円板, 棒のアスペクト比は 12 で計算され, マトリックスのじん性値を基準にとってある。

Figure 3. Plot of the Relative Toughness Versus Fraction in Volume of the Second Phase for a Composite

Key:

1. The aspect ratio of the disk and the rod is assumed to be 12 and the value of the toughness of the matrix taken as the standard.
2. Relative toughness
3. Fraction in volume
4. Rod
5. Disk
6. Sphere



- (1) ウイスキー5,6においてクラックブリッジングが引き抜きにより生じており、高じん化に寄与している。

Figure 4. Diagram for the Phenomenon of the Pull-Out of Whisker

Key:

1. Crack bridging due to the pull-out of whisker takes place at whiskers 5 and 6, thereby contributing to a higher toughness.
2. Crack
3. Whisker

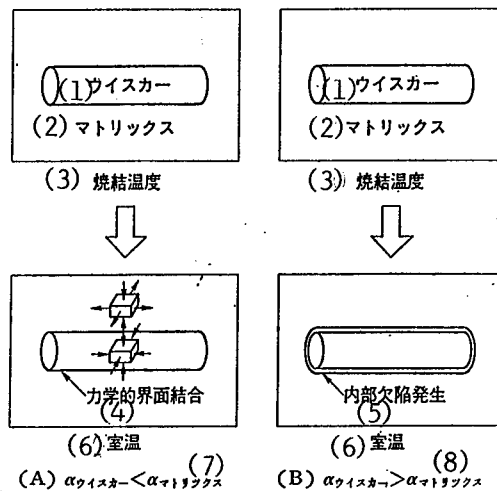


Figure 5. Diagram for the Development of (A) the Mechanical Bonding at the Interface and (B) Internal Defects at the Interface by Virtue of the Difference in the Coefficient of Linear Expansion

Key

1. Whisker
2. Matrix
3. Sintering temperature
4. Mechanical bonding at the interface
5. Development of internal defects
6. Room temperature
7. α whisker smaller than α matrix
8. α whisker larger than α matrix

toughness of a composite by means of crack deflection, providing the interface involves firm mechanical bondage.

The effect of the pull out of whiskers,^{4),5)} in turn, is illustrated in Figure 4. Providing that whiskers are of high strength and that the matrix whisker interface involves mechanical bonding, the bondage at the interface is weakened by the stress field at the crack-front and the phenomenon of a pull-out of whiskers occurs. In the vicinity of the advancing crack-front whiskers then serve to bridge the gap of the crack, thereby reducing, in a great measure, the stress concentration at the crack-front and enhancing toughness of the composite. The above mechanism presupposes an interface of two phases mechanically bonded and such a bonding of the interface, in general, is brought out only by a limited number of matrix-whisker couplings, that satisfy certain conditions.

2.2 Matrix-Whisker Couplings Permitting a Mechanical Bonding of the Interface

The conditions for obtaining a mechanical bonding of the interface between a matrix and a whisker are:

Condition (5): $\alpha_{\text{matrix}} > \alpha_{\text{whisker}}$

where α_{matrix} and α_{whisker} denote the coefficients of linear expansion for the matrix and the whisker, respectively.

Condition (6): No reaction products are formed at the matrix-whisker interface at temperature of sintering that provides true density.

In the coupling of a matrix and a whisker satisfying the conditions 5 and 6, a compressive stress on the whisker side in the vicinity of the interface and a tensile stress on the matrix side there develop upon cooling of the composite from the temperature of sintering to that of the ambient; thereby a mechanical bondage of the interface is produced. Where the inequality sign for condition (5) is reversed, a tensile stress develops at the interface upon cooling of a composite from the temperature of sintering to that of the ambient, sometimes leading to an internal defect; no mechanical bondings of the interface develops (see Figure 5).

2.3 Upper Limit of the Size of Whiskers

Even if the conditions (5) and (6) above are satisfied in the coupling of a matrix and a whisker, microcracks develop on the matrix side of the matrix-whisker interface if internal tensile stress occurring in the matrix is excessive, thereby reducing, again, the mechanical bonding of the interface. The condition for blocking such a development of unintended microcracks is the following:

Condition (7): The diameter of the whisker shall be below a certain critical value.

The condition for the development of microcracks upon cooling of a composite from the temperature of sintering to that of the ambient, in turn, is given by the formulas

$$\begin{aligned} R &\geq R_c & (1) \\ R_c &= \beta K_{Ic}^2 / \sigma_I^2 & (2) \end{aligned}$$

where R is the diameter of the whisker, R_c the critical diameter of whiskers for the development of microcracks, β a constant of $2\sqrt{4}$, K_{Ic} the fracture toughness of the matrix, and σ_I the tensile stress developing on the matrix side of the matrix whisker interface.

Assuming that the maximum internal stress developed at the interface by the difference in the coefficient of linear expansion between the matrix and the whisker is made up exclusively of plane stress, the σ_I is given by

$$\sigma_I = \frac{E\Delta\alpha\Delta T}{(1+\nu)} \quad (3)$$

where E stands for Young's modulus, $\Delta\alpha$ the difference in the coefficients of linear expansion between the matrix and the whisker, ΔT the difference between the temperature of sintering and that of the ambient, and ν Poisson's Ratio. From the formulas (1), (2), and (3) the conditions for the development of microcracks may be represented by

$$\begin{aligned} R &> R_c & (1') \\ R_c &= \frac{\beta K_{Ic}^2 (1+\nu)^2}{E^2 (\Delta\alpha)^2 (\Delta T)^2} & (4) \end{aligned}$$

R_c , therefore, can be calculated when relevant values for the matrix and the whisker are known and the temperature of sintering given. It is evident from these formulas that the diameter of the whisker shall be below R_c if development of microcracks are to be blocked. It is, therefore, critically important that a whisker of a diameter as small as possible be used in order to prevent the development of microcracks due to a difference in thermal expansion.

2.4 Controlled Chemical Bondage at the Matrix-Whisker Interface

In the foregoing discussion, the authors presupposed that an exclusive mechanical bondage at the matrix-whisker interface is desirable. They argued that the selection of a matrix and a whisker to be coupled and selection of the size of the whisker be made for the best control of this bondage, if a toughening of a composite by means of whisker is to be effective. Alternatively, however, it may be assumed, by easing the above condition, that a method of manufacture is yet possible wherein the matrix-whisker interface involves a chemical bonding the force of which, nevertheless, is under control. The intriguing consequences that must follow are:

First, the force of bonding at the interface may then be varied as desired by control of the chemical bonding force at the interface, whereas, in cases where mechanical bonding force alone is involved at the interface, the matrix is subjected exclusively to tensile stress and the whisker subjected to compressive stress. An optimum condition may possibly be produced at the

interface of a ceramic composite, just as Al-Cu alloy has the hardest consistency when the precipitate is intermediate between the matched or coherent one and the one that is not.

It may conceivably also be possible here that the consumption of the fracture energy in the cleavage of the chemical bonding at the interface which must take place in the stress field of the advancing crack front contributes to raising the toughness of the composite as do the mechanisms of the crack deflection and the pull-out of whiskers.

In the second place, even in the coupling of a matrix and a whisker that does not meet the condition (5) above, it may be possible to block the development of tensile stress at the interface and formation of internal defects that take place upon cooling of the compact from the temperature of sintering to that of the ambient, providing that an appropriate chemical bonding is provided to the interface. It is expected, at this juncture, that the interface bondage may display multifarious intriguing phenomena in the stress field of an advancing crack front.

In cases where the force of chemical bonding at the interface is excessive in contrast to the above, the stress field of an advancing crack front does not produce a reciprocal action on the force of bonding at the interface but the crack runs through the whisker. The crack deflection and the pull-out of whiskers that contribute to the toughening of the composite hence fail to take place. It is, therefore, essential that "a force of chemical bonding well controlled at the interface" be aimed at.

Such "a force of chemical bonding well controlled at the interface" may conceivably be produced by means of some coating over the surface of whiskers, an appropriate selection of the temperature of sintering, etc. Though the importance of the issue of the interface such as the above has not yet been well understood, it must make an important key factor in future in the development of a ceramic composite.

2.5 Dispersion of Whisker

The question of how to disperse a whisker appropriately in a matrix makes the one of the highest importance in the manufacture of the composites because the strength of the composite is affected gravely by the development of defects due to the tangling of whiskers and by the distance between whiskers.

The strength against fracture, σ_f , is generally given by

$$\sigma_f = \frac{K_{Ic}}{Y\sqrt{a}} \quad (5)$$

where K_{Ic} stands for the fracture toughness of the composite, Y the geometrical factor of the fracture source, and a the maximum fracture source. Tangling of whiskers, if there is any, makes a source of fracture, thereby raising the value of a and diminishing the strength, as does non-homogeneous dispersion of whiskers, which produced areas lacking in whiskers. Figure 6 [omitted] shows a result of the experiments conducted by the authors:^{8),9)}

Table 1. Difference in Mechanical Property at Room Temperature of Ceramics Between Those Combined with SiC Whisker to Form a Composite and Those Not

Ceramic Composite	Strength (MPa)	Fracture Toughness (MPa-m ^{1/2})	Reference
Si ₃ N ₄	600~ 800	5 ~ 6	11)
Si ₃ N ₄ /SiC(W)*(10~50) ^{2*}	590~ 680	-	13)
Al ₂ O ₃	500	4	11)
Al ₂ O ₃ /SiC(W)(20)	800	8.7	14)
Al ₂ O ₃ /ZrO ₂ (TZP) ^{3*} (0~50)	500~1,100	5 ~ 8	9)
Al ₂ O ₃ /ZrO ₂ (TZP)(15)/ SiC(W)(15)	1,100~1,400	6 ~ 8	8)
Mulite	244	2.8	10)
Mulite/SiC(W)(20)	452	4.4	10)
Mulite/ZrO ₂ (TZP)(10)/ SiC(W)(20~30)	551~ 580	5.4~ 6.7	10)
Cordierite	180	2.2	10)
Cordierite/SiC(W)(20)	260	3.7	10)
Cordierite/ZrO ₂ (TZP)(20)	190	-	10)
Cordierite/ZrO ₂ (TZP)(20)/SiC(W)(20)	380	-	10)
3Y-TZP ^{4*}	1,150	6.8	10)
3Y-TZP/SiC(W)(20~30)	590~ 610	10.2~11.0	10)

* SiC whisker

^{2*} Figures in parenthesis is in percent in volume

^{3*} Tetragonal Zirconia Polycrystal

^{4*} 3 mol percent Y₂O₃ TZP

in picture (A) where dispersion is poor, some regions are devoid of whiskers, contributing to the fall of strength.

2.6 Other Mechanisms of Toughening and Their Additive Property

Coupling of a ceramic matrix with a high-elasticity whisker conceivably makes the composite tougher by the mechanisms of crack deflection and the pull-out of whiskers; besides these, however, have been suggested the following relevant mechanisms: (a) toughening by transformation; (b) toughening by microcracks; (c) toughening by crack bridging based on the capacity for plastic deformation. Mechanisms (a) and (b), of these, are described in detail in this feature articles issue by Sato and Shimada and by Miyata, respectively. The mechanism (c) takes place in cases where the second phase is capable of undergoing plastic deformation. The second phase remains unbroken by virtue of its relevant capacity when a crack passes through that phase. It thus acts to bridge the gap produced by the crack, a mechanism essentially identical with that of the pull out of whiskers.

Of the above three mechanisms (a) and (c) must be compatible with the mechanisms of toughening by whiskers and hence provide high additive value of toughening. The designing of raw materials for a ceramic composite in which a plural number of toughening mechanism work in an additive manner must be aimed at as a future problem. In mechanism (b), in contrast, microcracks, developing in the stress field of the very main crack, act to diminish the mechanical and chemical bonding forces between the matrix and the whisker. In other words, toughening of a composite by whiskers and by microcracks are not compatible with one another and, hence, one cannot count on a combined effect of toughening from these mechanisms.

3. Present Status for the Toughening of Ceramics by Whiskers

Since the toughening of ceramics by whiskers, as described above, is very effective, research on the relevant subject has been energetically pushed ahead recently in the West as well as in Japan.¹⁰⁾⁻¹⁴⁾ The case of the SiC whisker, which has yielded intriguing results as given in Table 1, follows:

3.1 Si₃N₄/SiC-Whisker Group

This group is studied with the view to improving the fracture strength, at high temperatures, of Si₃N₄ on the basis of high elasticity and high resistance to heat of SiC whisker.^{12),13)} The product obtained has an improved strength at high temperature, i.e., 650 MPa at 1,300 degrees C and displays an excellent Weibull coefficient $m = 25$, though its strength at low temperature is decreased. The composite resulting meets the aforementioned condition (1), the dispersion of whisker, condition (3), the longer elongation at fracture of the matrix than that for whisker, and condition (7), the diameter of the whisker smaller than the critical one. But it perhaps does not meet the conditions (2), (5), and (6), wherein condition (2) is equivalent to those of (5) and (6). In this composite system

$$\alpha_{\text{Si}_3\text{N}_4} < \alpha_{\text{SiC}} \text{ whisker} \quad (6)$$

in the first place. This implies that the matrix and the whisker are coupled in such a way that a tensile stress on internal defects may develop at the interface upon cooling of the sintered products to room temperature. The SiC whisker involved serves just to bring in defects. The very high value of Weibull coefficient may conceivably be due to a very small value of the variance of the size of the defects developed, which, in turn, results from a small value of the variance of the size of whiskers dispersed.¹³⁾

Second, this composite system contains sintering assistants of the oxide type because Si_3N_4 and SiC are not subject to sintering and, hence, a substantial amount of grain boundary impurity phase must possibly be present at the matrix-whisker interface. Products involving the assistant which is added not because it produces "a controlled chemical bonding at the matrix-whisker interface" but because it enhances sintering, has perhaps failed to forego the effect of the internal defects developed at the matrix-whisker interface and, hence, has a lower strength at room temperature than for the simple Si_3N_3 compact.

The improvement in strength and toughness of this composite system seems to be dictated by whether or not an interface-phase involving a controlled chemical bonding is formed at the Si_3N_4 -SiC whisker interface. This bonding may conceivably be accomplished, to be more precise, by devising either a sintering assistant that enhances the interface bonding at the Si_3N_4 -SiC whisker interface or a coating of the surface of SiC whisker with a substance that enhances its attachment to the Si_3N_4 and a sintering that follows.

3.2 Composite Involving Al_2O_3 and 20 Percent in Volume of SiC Whisker

Composites of this group have been examined by Becher, et al.,¹⁴⁾ who have obtained values for fracture toughness of $8.7 \text{ MPa}\cdot\text{m}^{1/2}$ and fracture strength at room temperature of around 800 MPa for a specimen that had been subjected to hot pressing at 1,850 degrees C and which was ruptured vertically to the direction of the orientation of its whiskers. They concluded that the dispersion of SiC whiskers and non-flocculation of the matrix alumina are factors of maximum importance in raising the strength and the fracture toughness.

When the conditions for obtaining ceramics of high toughness above are referred to in connection with these results, condition (1), or the dispersion of whiskers, may conceivably be satisfied fairly well because of the use of the supersonic dispersion. Condition (2), or the mechanical bonding at the interface also may be satisfied anyhow because the condition (4) of Al_2O_3 -SiC whisker is met as condition (5) by non-use of sintering assistant. Finally, condition (6) or the diameter of whiskers involves no problem. From above reasons, a composite comprising SiC whisker and Al_2O_3 may well have an excellent toughness and strength in comparison with the compact exclusively made of Al_2O_3 .

There is the possibility, nevertheless, of some reaction product arising at the interface between the Al_2O_3 and the SiC whisker which produces a firm chemical bonding there. The author et al., have found fractured surfaces where the crack runs through whiskers without taking deflected courses in a

specimen of a composite of the same group subjected to hot pressing at 1,800 degrees C because of an extremely strong bondage occurring at the interface between the Al_2O_3 and the SiC whisker.⁸⁾ (refer to Figure 7 [omitted as directed]) There is yet no denying the possibility that these fractured surfaces resulted from the difference in the kind of the whiskers used and, hence, from the difference in their purity and surface condition and, in particular, in the SiO_2 film over the surface of the whiskers.

Anyway, the success in this composite group is evidence that the conditions for obtaining a ceramic composite of high toughness described above are appropriate ones. The authors, et al.,^{8),9)} developed this group of composites further and selected a system comprising the Al_2O_3 matrix, SiC whiskers, and ZrO_2 (TZP) which follows:

3.3 Composites Involving Al_2O_3 , 15 Percent in Volume of SiC Whisker, and 15 Percent in Volume of ZrO_2 (TZP)

This system of composite materials has been studied with the aim of combining, in an additive manner, the effect of toughening a ceramic by the mechanisms of crack deflection and pull-out of whiskers and the one by the mechanism of transformation involving use of whiskers and zirconia, respectively, as referred to in Section 2.6. The volume fraction of SiC whisker has been set at 15 percent on the basis of the calculation of Faber, et al.,³⁾ (See to Figure 3) and that of ZrO_2 (2 mol percent Y_2O_3 also at 15 percent allowing for the result of research on the Al_2O_3 - ZrO_2 system by Claussen, et al. The assessment of this system by the conditions (1) to (7) for the toughening of composite materials by whisker given above is the following:

(a) Dispersion of whisker, condition (1)--the authors, et al., made research on the blending of Al_2O_3 , ZrO_2 , and SiC whisker and successfully produced a uniform dispersion of the whiskers which are approximately of equal length as shown in Figure 8 [omitted].

(b) Generation of a mechanical bonding force at the interface, conditions (2), (5), and (6)--in this system we have

$$\propto Al_2O_3, ZrO_2 > \propto SiC \text{ whisker} \quad (8)$$

In addition, with no sintering assistant added, formation of a reaction product at the interface does not seem possible. In consequence, we conclude that mechanical bonding force is generated at the matrix-whisker interface.

(c) Elongation at fracture of the matrix larger than that for the whisker, condition (3)--the elongation, at the time of fracture, of SiC whisker is approximately equal to that for the matrix Al_2O_3 - ZrO_2 . An effect of the load transfer as large as those for FRPs and FRMs, hence, is not possible; the effect, nevertheless, must be produced in any part of the matrix-whisker interfaces except in areas where the crack has broken down the mechanical bonding because the Young's modulus of SiC is one and a half times to twice as large as that for Al_2O_3 - ZrO_2 and because the mechanical bonding has been produced at the interface.

(d) Diameter of the SiC whisker below the critical one, condition (7)-- Whereas the critical diameters of whiskers that permits development of microcracks is around 5 microns as computed from formula (4), the actual diameter of the whisker used is below 1 micron; no question, hence, is involved in connection with this condition.

As can be seen from the above, the conditions for toughening of a ceramic by whisker seem to be fulfilled in a large measure.

Where the effect of ZrO₂ is concerned, the toughening effect based on transformation very conceivably must have taken place, as pointed up by Claussen, et al., since the grain diameter is of the order of 0.5 micron [Figure 6 omitted] and since the difference in the quantity of the monoclinic system between the polished surface and the fractured surface is above 10 percent as determined by the x-ray quantitative analysis. Another important effect of ZrO₂ grains is that the grain, located at the triple point of the Al₂O₃ crystal grains and preventing the Al₂O₃ crystal grain from getting crude and large, produces a very fine texture.

The authors, et al.,⁹) have recently attained a maximum strength of 1437 MPa at room temperature by combining the above effects with a special processing after the hot pressing, that is, a surface processing and a special heat treatment in that order. Such a high strength is attained conceivably because of the success in producing the following effects in one composite material in the additive manner: the effect of the load transfer by SiC whisker, the effect of crack deflection, the effect of the pull-out of whisker for toughening; the effect of the ZrO₂ for transformation toughening and for the fine texture of the crystal grain; the effects of a surface processing and a special heat treatment.

4. Problems Posed and Future Prospects

Whisker-reinforced composite material requires the use of whiskers of high strength and high elasticity. Ceramic whiskers commercially available at present, nevertheless, are limited largely to those of SiC and Si₃N₄ and these whiskers have to be coupled only with the matrix of an oxide such as Al₂O₃ or ZrO₂ if the condition (5) $\alpha_{\text{matrix}} > \alpha_{\text{whisker}}$, the most important for a composite material, is to be met. For this reason, the range of temperatures available for this composite when used as high-temperature structural material is very limited.

If SiC or Si₃N₄ is chosen as the matrix material in order to develop a high-temperature structural materials of composite structure available at temperatures above 1,300 degrees C, SiC whisker to be coupled with cannot afford to meet the condition (5); it thus fails to produce the mechanical bonding at the interface and hence to provide toughening effect. This can be solved only if "a controlled chemical bonding at the interface" is produced.

Characterization of the matrix whisker interface, the most important site in a composite material, is very difficult, however. The interface, of the order of scores of angstroms in thickness, is resisting highly sophisticated technologies, even the use of the transmission type of the analytical electron

microscope, in regard to the question of what exists and how it exists in this interface. It is difficult, therefore, to tell whether the bonding force produced at the interface is a mechanical or a chemical one--a question which seems to present a major snag in the development of composite materials. The question for the cause of the bonding force at the interface and for the method of relevant assessment will make a major item of research on the development of composite materials in the coming years.

Another problem involved is that the type of whiskers available is very limited and that the research on surface modification has not yet been made adequately. Emergence of whiskers with unique properties is eagerly awaited on the one hand, and modification of the surface of whiskers by means of solution treatments, CVD, PVD, etc. such that the whisker matches or becomes coherent to the matrix makes an important subject of research on the other.

The final problem is that of the dispersion of whisker at the time of manufacture. As far as ceramic composites reinforced with whiskers are concerned, the problem of the dispersion of whiskers is one that must confront the relevant researcher throughout his work because, if he devises a method of dispersing very fine whiskers in a large volume proportion without involving defects due to tangling, etc., he may reasonably hope for a product of substantial strength and toughness even if the matrix is of low toughness, e.g. a glass matrix.

5. Conclusion

As described above, the dispersion of whiskers in a ceramic has proved to make a very effective means of toughening providing that a matrix and a whisker to be coupled are carefully selected. Nevertheless, the researcher now has to confront new problems, which he seldom encountered in connection with a single-phase ceramic, e.g., the dispersion of whiskers, the bonding at the interface, and orientation of whiskers. The last being not referred to above. The development of new whiskers, that of some unique idea for coupling them with a matrix, and that of new manufacturing technologies that substantiate the idea may conceivably be of importance if these problems are to be solved and to be further evolved.

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CHARACTERISTICS OF AMORPHOUS ALLOY POWDERS DISCUSSED

Tokyo KINO ZAIRYO in Japanese Aug 86 pp 51-60

[Article by Fumio Motegi, director, Research and Development Division of Riken, Ltd., and Hiroyoshi Ishoi, member, same division; first paragraph is editorial introduction]

[Text] Amorphous alloys have been spotlighted as fantastic metals since they exhibit excellent magnetic, chemical, and mechanical properties. This paper briefly deals with various characteristics of the amorphous-alloy powders developed with a view to expanding the application of amorphous alloys and, further, with those of molded bodies produced by secondary processing of the powder.

1. Introduction

Amorphous alloys, which are the opposite of perfect crystal metals, are not known to occur in nature, for the most part, and their nonequilibrium phase is produced artificially. It is also known that they have an irregular atom structure, leading to peculiar properties. Though they have long been referred to as a fantastic metal, they have found applications only to a limited extent, including magnetic heads and radio frequency cores. There is no denying, in this connection, the fact that the shape of the thin ribbons of this substance is partly responsible for this phenomenon.

Amorphous alloy powders have been developed with a view to expanding multifarious applications of amorphous alloys based on their characteristics. In other words, amorphous alloy powders can be shaped freely and hence can find applications either in powdered form or in complex forms when the powder is subjected to secondary processing or molding.

2. Methods of Manufacturing Amorphous Alloy Powders

The cooling rate required for the manufacture of amorphous alloys, which varies with the composition of the alloy, is generally $10^4 - 10^6$ K/sec; thus amorphous alloy production is too sophisticated for general industrial manufacturers. The manufacture of this ribbon, which is accomplished with the single roller method, etc., is carried out with the cooling rate controlled by solidifying the melt with a rotating metal roller.

The cooling speed is of major importance when manufacturing amorphous alloy powder. Though a number of methods have been studied, no one has yet been able to attain technology at the industrial level because of limited compositions and restrictions such as changes in states with varying grain diameters. Striving to upgrade the technology to the industrial level, Riken, Ltd., jointly with Tohoku University, developed the cavitation method which allows alloys to attain an amorphous state regardless of the grain size of the alloy. As shown in Figure 1, the method basically is made up of the three processes of dissolution, atomization, and solidification. The twin rollers at the center are made from substances of low wettability, such as graphite or ceramic, and rotate in the directions indicated at a high speed so that the melt passing between the rollers are mechanically atomized (cavitation phenomenon) and turned into melt drops, which collide with the rotating metallic rollers set below and convert to the amorphous state. This method features a high degree of cleanliness on the surface because of the dry manufacturing process and easy control of the relevant temperature because of the short distance between the atomization rollers and the solidification roller. Since the cooling speed of the melt-drops is dictated by the rolling metal rollers, the conditions for manufacturing are basically similar to the ones for ribbons, affording a wide range of alloy compositions amenable to amorphous-state formation. The shape of the powder obtained varies with manufacturing conditions, but is largely in flake or plate form with large aspect ratios.

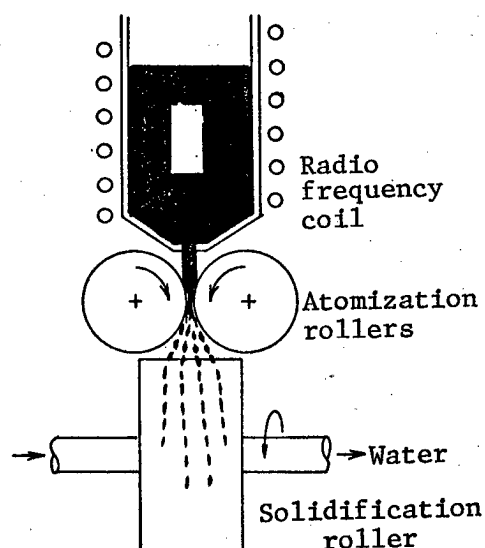


Figure 1. Diagram of Cavitation Machine

Photograph 1 [omitted] presents electromicroscope pictures of representative amorphous powders. Photo shows superfine amorphous particles prepared by the sputtering method, instead of the cavitation method, which is being developed by the Research Development Corp. of Japan.

3. Characteristics of the Powder

Characteristics of the powder are presented in Figure 2. Although the characteristics of the powders vary considerably with the composition and the shape of the particle, those shown in the figure are of a powder composition $(\text{Co} + \text{Fe})_{73}(\text{Si} + \text{B})_{27}$ and have plate and semispherical forms. The grain size values plotted in the figure, meanwhile, represent medians for the individual ranges of grain diameters measured. The specific surface area of the grain grows larger with a decrease in the diameter of the grain and has a value of $0.9 \text{ m}^2/\text{g}$ for a grain diameter 5 microns and under, a value two digits larger than for thin ribbons. Some amorphous alloy powders of nickel exhibit a value of several square meters per grain and superfine particles, as indicated in Photograph 1(e) [omitted], have a value larger by one digit. Secondly, the plot of the caloric value of the heat generated with regard to the diameter of the grain shows that the caloric value begins to fall when the diameter drops below 21 microns. It has also been found, though not shown, that the temperature of crystallization tends to decline when the diameter falls below 6 microns. Thirdly, flowability (JIS 2502), apparent density, and tap density (JIS 2504), which represent basic properties of the powder, are found to be mutually correlated and vary with the shape of the powder. A powder in plate form has a fluidity of 30 seconds and a tap density of 4.1 g/cm^3 , the maximum in a grain diameter range of 44 to 74 μm , whereas powder in semispherical form has a flowability of 19 seconds and a tap density of 5.0 g/cm^3 , the peaks in a diameter range of 20 to 44 μm . The flowability rapidly declines when the grain diameter falls below 21 μm , thus lowering the apparent and tap densities as well. This results from the shape changes of the particle and substances absorbed, which is largely water. In terms of thermogravimetry, one finds the weight falls more as the particle diameter decreases; there is a weight change of around 0.6 percent at diameters below 6 μm .

A discussion on relevant catalytic and magnetic properties follows.

3.1 Magnetic Properties

Amorphous alloys have no crystal anisotropy, have a very low coercive force, and exhibit characteristics of the softest magnetic material in existence. Their powdered products, nevertheless, behave in quite different manners. Figure 3 shows measurement results using a vibrating sample magnetometer at 10 kOe [kilo Oe] for the powders $(\text{Co} + \text{Fe})_{73}(\text{Si} + \text{B})_{27}$ and $\text{Fe}_{75}(\text{Si} + \text{B})_{25}$. The magnetizing force tends to drop with decreases in the grain diameters of the powders, which can be inferred on the ground that the specific surface area increases and the quantity of heat drops with decreases in grain diameter, as plotted in Figure 2. The dependence of the magnetizing force on grain diameter is relatively less for the Co powders, but remarkable in those of Fe powders. When subjected to heat treatment at 200°C – 400°C , however, powders with smaller grain diameters restore their magnetizing force to some extent. The coercive force of the powder, in contrast to the magnetizing force, tends to grow with decreasing grain diameter, though Fe and Co powders differ from one another in the manner in which these changes are exhibited. Co powders increase their coercive force

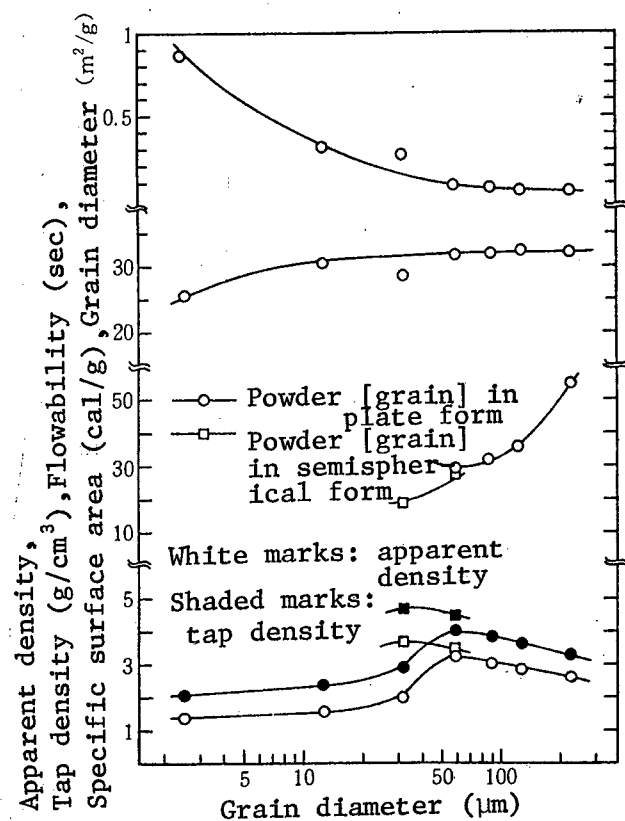


Figure 2. Plot of the Grain Diameter of the Powder With Regard to Specific Surface Area, the Quantity of Heat Generated, Flowability, Apparent Density, and Tap Density

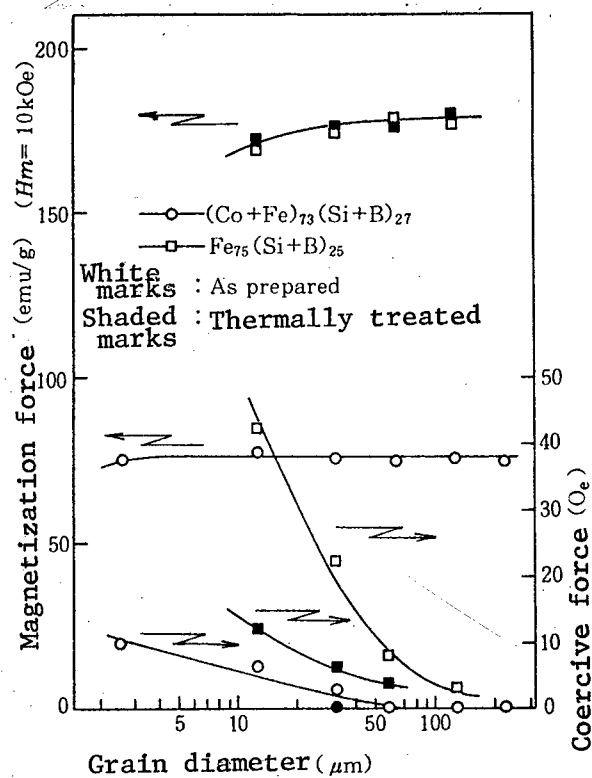


Figure 3. Plot of Powder Grain Diameters With Regard to Magnetization Force and Coercive Force

gradually with declining grain diameter, with the value staying at 10 Oe for a grain diameter below 6 μm , whereas the value of Fe powders varies greatly with grain diameters of 44 μm and under with a coercive force as large as 45 Oe for a powder with grain diameters of 5 to 20 μm . When subjected to appropriate heat treatment, however, the coercive force of the powder falls for each grain diameter; for Fe powders with grain diameters of 5 to 20 μm ; down to 12 Oe, which, nevertheless, is larger than for Co powders. Superfine amorphous particles of Fe-B with grain diameters 0.2 μm and under, pictured in Photograph 1(e) [omitted], meanwhile, have an extremely large coercive force of 400 Oe. It may be said that amorphous alloy powders begin to shift from soft magnetic material characteristics to hard magnetic material ones at grain diameters of 20 μm and under.

Examples of the applications of amorphous alloy powders, which are based on their characteristics plotted in Figures 2 and 3, follow.

3.1.1 Powders for the Electromagnetic Clutch

The electromagnetic clutch of the magnetic powder type transmits torque from the drive part to the part to be driven through an intervening magnetic powder and is capable of transmitting a constant torque irrespective of the relative number of rotations in the two parts involved. The critical element in this type of clutch is the magnetic powder, which is required to have soft magnetic material properties, high magnetic flux density, and high resistance against abrasion and corrosion. Semispherical amorphous alloy powder, Photograph 1(c) [omitted], in turn, exhibits very high flowability and high tap density, in addition to high permeability, high hardness, high toughness, and high resistance to corrosion, and hence is the appropriate powder for the electromagnetic clutch. The powder that has a semispherical shape with a certain aspect ratio is favored over spherical powders in terms of magnetics; it affords a high torque while ensuring smooth slip characteristics. The high permeability of the powder, in addition, permits the reduction of the magnetic current and hence the size of the device.

3.1.2 Powders for Magnetic Polishing

Magnetic polishing involves the arrangement of a magnetic powder between electrodes to form a magnetic brush and polishing workpieces with the brush to produce a mirror surface. The powders for this magnetic brush must be of soft magnetic material and be capable of polishing. Until the discovery of amorphous alloy powders, a powder combining these two properties had not been available and powders of composite materials were used; the amorphous alloy powder, in turn, is a superior soft magnetic material and is of a high hardness (Hv 600 to 800) and high toughness, the magnetic powder for polishing. Figure 4 presents the quantity polished off from a quenched material SK-3 by using amorphous alloy powders. The amount polished off is larger for the powder $(\text{Co} + \text{Fe})_{73}(\text{Si} + \text{B})_{27}$ of low magnetic flux density than for the powder $\text{Fe}_{75}(\text{Si} + \text{B})_{25}$ of high flux density and a mirror surface is imparted to the workpiece in a short time. Amorphous alloy powders do not inflict deep cuts on a workpiece when polishing because of the lack of sharp edges and hence are best for applying the ultimate finishing polish.

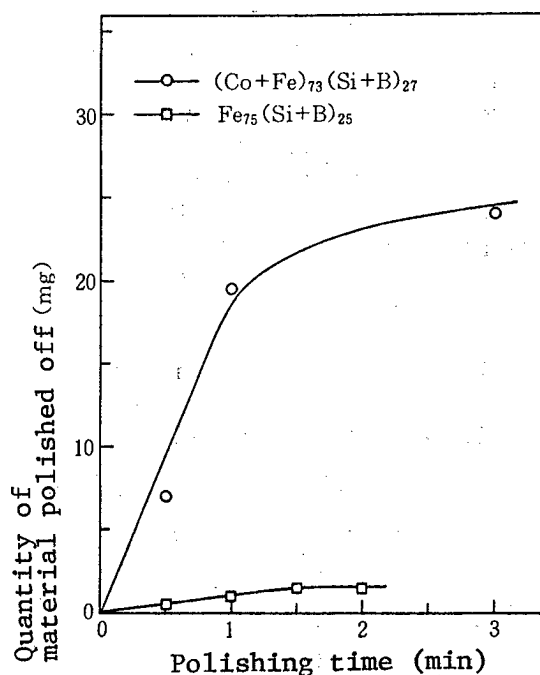


Figure 4. Plot of Polishing Time Versus the Quantity of the Material Polished Off

Their high permeability and high tap density also permit a smaller external magnetic field and thus a more compact apparatus.

3.2 Catalytic Characteristics

Because of their structural features, amorphous alloys represent materials of new properties in the field of chemistry including catalysts. Their catalytic properties, in particular, include features lacking in crystalline materials. As pointed out, however, they involved difficulties in their practical application resulting from their shape, for example, low per-unit-weight activity. Amorphous alloy powders, in turn, are capable of having their specific surface area raised to over $1 \text{ m}^2/\text{g}$ by reducing their grain diameters, as given in Figure 1, and hence, may be put to practical application as a catalyst. The following are the catalytic properties, for the hydrogenation of unsaturated hydrocarbons, of amorphous alloy powders, which are aimed at superseding noble metal catalysts and Laney's catalyst.

3.2.1 Hydrogenation of Butadiene

The conjugated double bonds of 1,3-butadiene are hydrogenated with the use of Ni-Zr amorphous alloy powder; the reaction formula is given in the figure.

Figure 5 presents the selectivity (of reaction sites) in the hydrogenation of butadiene: Ni-Zr amorphous alloy powder (a) exerts a similar effect to that of Pd(c), which is shown for comparison. The plot indicates that the

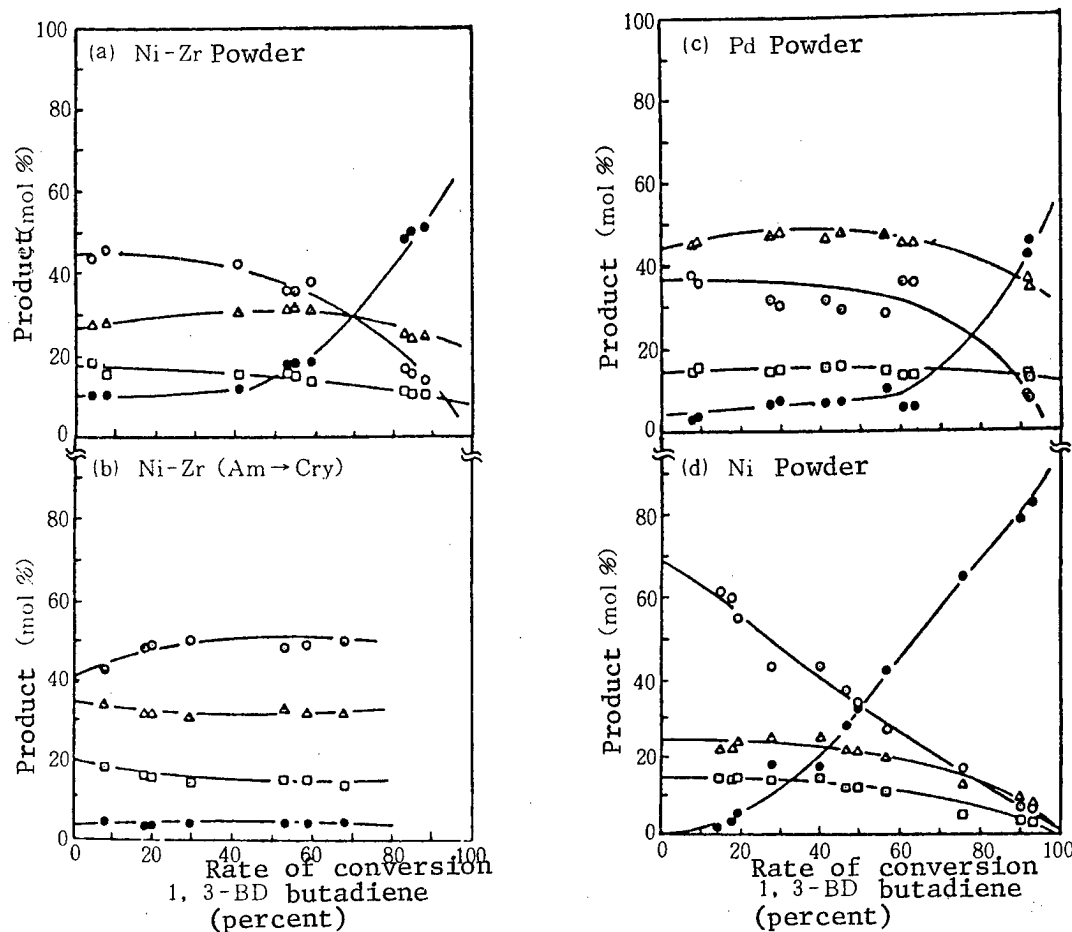


Figure 5. Hydrogenation of Butadiene by Means of Various Catalysts

yield of n-butane is limited even if the percentage of conversion of butadiene is raised and that the catalyst, hence, exhibits high selectivity for the formation of butenes. Since nickel (a) alone does not show such selectivity for butenes, the selectivity must be a result of alloy formation. It must also be noted that the Ni-Zr crystals produced by the crystallization of its amorphous alloy powder (b) exhibits still higher selectivity, indicating that the method of preparation is a decisive factor for producing superior catalyst materials.

3.2.2 Hydrogenation of Styrene

Figure 6 presents characteristics of the $\text{Ni}_{75}(\text{Si} + \text{B})_{25}$ amorphous alloy powder, its thin ribbon, and Raney's nickel for the hydrogenation of styrene. The $\text{Ni}_{75}(\text{Si} + \text{B})_{25}$ thin ribbon, though subjected to filing prior to entering the reaction, has a very slow reaction rate and produces only a limited reduction in the relevant hydrogen pressure. The amorphous alloy powder of the same composition, in turn, behaves differently, producing a major

reduction in the pressure in a short time. The amorphous alloy powder with a specific surface area of $6 \text{ m}^2/\text{g}$ has a drop rate in hydrogen pressure nearly equal to that for Raney's nickel with a specific surface area of $60 \text{ m}^2/\text{g}$; this implies that the former has a catalytic activity per surface area 10 times that for the latter and will be an epoch-making catalytic material if its specific surface area is expanded further.

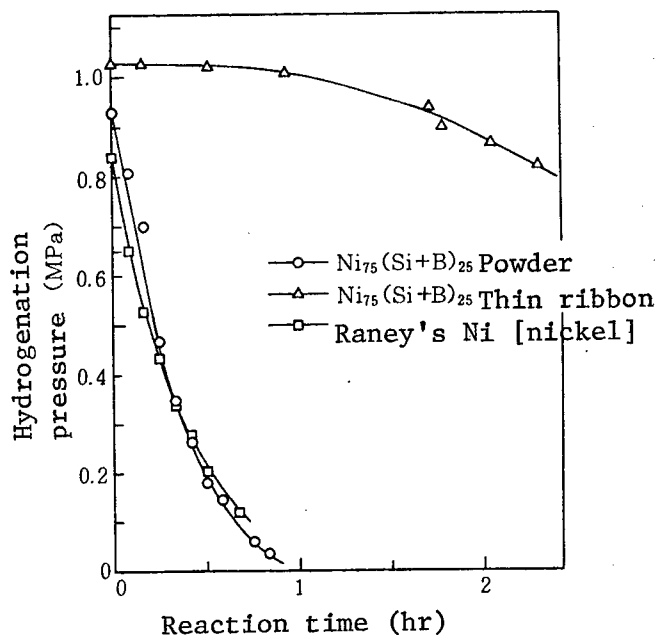


Figure 6. Pressurized Hydrogenation of Styrene by Means of Various Catalysts

4. Characteristics of the Molded Body of the Powder

Amorphous alloy powders may be molded into various shapes by applying different molding technologies. Representative properties of molded products follow.

4.1 Unadulterated Molded Bodies

Unadulterated molded bodies of an amorphous alloy powder may be produced by such means as hot pressing and HIP; nevertheless, they lack sufficient strength since the thermal instability of the powder, which is its greatest demerit, does not permit the application of enough heat to raise the temperature to the level where atoms migrate. A special method referred to as impact pressure aggregation, on the other hand, has been found to produce an unadulterated molded body of high strength. This method involves the application of a wave of impact pressure at normal temperature: application of a pulse pressure of $10^4 - 10^5$ atmospheres that exceeds the limit of elasticity of the solid for a very short time of 10^{-9} seconds produces a compression similar to the one produced by hydrostatic pressure. The mechanism of the aggregation of an amorphous powder alloy involves a rise in temperature of

minor parts of the surface layer of the powder upon passing an impact wave generated by the impact pressure above, leading to melting of the surface area and aggregation of the powder; the amorphous state of the internal part of the powder is preserved by the subsequent cooling. It is of course necessary as a molding condition that the temperature maintained after the adhesion be lower than that for crystallization. The relevant conditions, as determined by Rankine Hygoniot's equation of state, vary largely with the initial density. Figure 7 presents the plot of impact pressure versus density, hardness, compressive fracture strength, and the quantity of heat generated up to crystallization, of the molded body at a 40 percent initial density. The molding is 99.9 percent and over of the true density provided the impact pressure is 5.5 GPa and over and has a hardness approximately equal to that of a thin ribbon. The quantity of heat generated is nearly constant for impact pressures 8 GPa and below and the X-ray diffraction picture is broad without a crystallization peak, indicating that the powder preserves its amorphous state. Where compression fracture strength is concerned, molding at 1.5 GPa is possible.

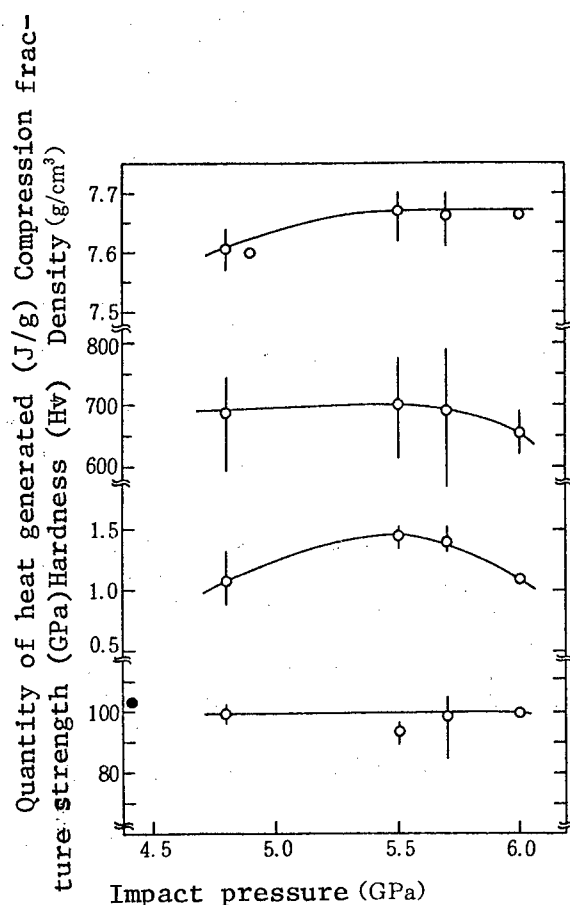


Figure 7. Plot of Impact Pressure Versus Density, Hardness, Compression Fracture Strength, and the Quantity of Heat Generated

Chemical Formula for the Hydrogenation of Butadiene

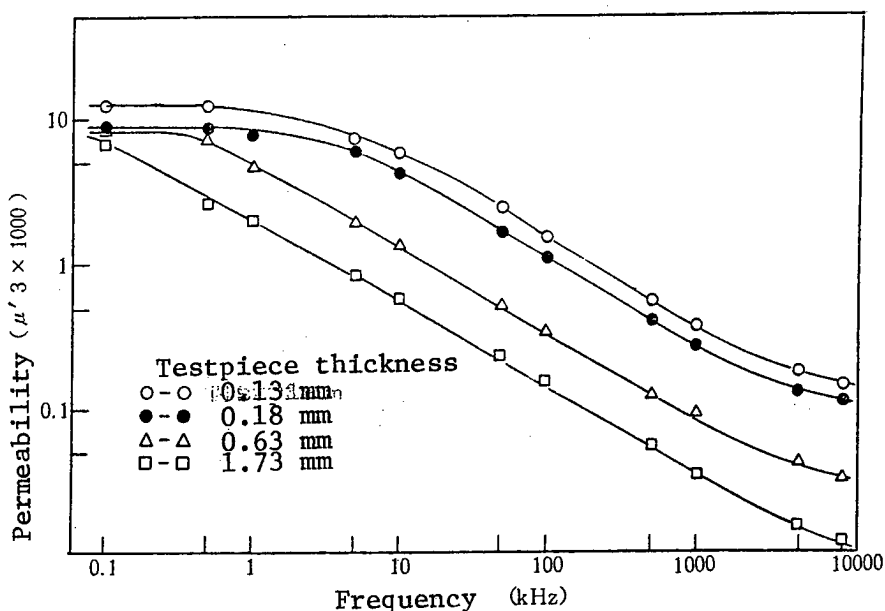
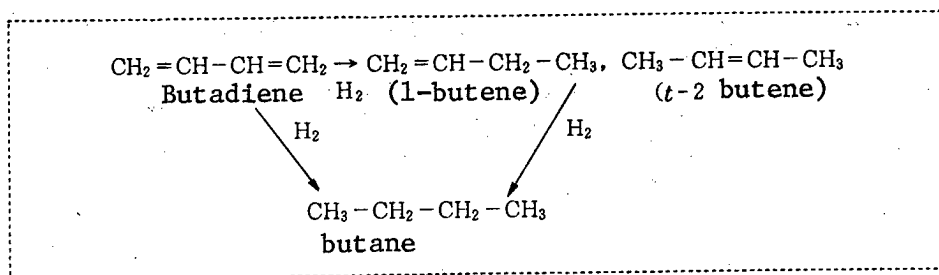


Figure 8. Plot of Permeability Versus Frequency for Testpieces of Different Thickness

A magnetic property, i.e., permeability of the amorphous alloy powder $(\text{Co} + \text{Fe})_{75}(\text{Si} + \text{B})_{25}$, in turn, is presented in Figure 8. A permeability of 12,000 for a thickness of 0.13 mm has been obtained, though the value falls with an increase in the thickness because of the loss in the eddy current. With regard to its direct current characteristics, the molding also displays a superior coercive force of 20 to 30 mOe. Still another feature is that a high permeability of 1 to 10 MHz is exhibited by a thin core 20 μm thick made of a piece of unadulterated molding of an amorphous alloy powder, which is suitable for VTR magnetic heads.

4.2 Resin Moldings

Amorphous alloy powders may be processed into various shapes by using resins as the binder.

4.2.1 Granules

An amorphous alloy powder may be molded, by means of a binder and a grain molding machine, into large grains, as shown in Photo 2 [omitted]. With the sphere in Photo 2(a) [omitted]. With the sphere in Photo 2(a) molded with powders with particle diameters of about 100 μm and that of Photo 2(b) with those with particle diameters of 10 μm and under, amorphous alloy powders are laminated in an orderly manner and the density of the moldings approaches the tap density.

Because of the lamination of its powder, the sphere surface is undulated and is an excellent magnetic particle for the separation of magnetic forces. In contrast to particles without undulated surfaces, these granules are provided with a magnetic gradient over the surface, leading to increased areas of capture and improved capture efficiency. The capture efficiency is nearly 100 percent, provided the magnetic particles to be captured are ferromagnetic. The granules also have the advantage that they are very easy to handle because of their granular form and that the entire system of devices may be made more compact because the amorphous alloy has a high permeability and hence a large external magnetic field is not needed. The binder must be selected properly according to the kind of liquid, temperature, and other conditions applied.

4.2.2 Cores of the Amorphous Alloy Powder Molded With Resin

Because of the high electrical resistance and high permeability of amorphous alloys, cores made by molding an amorphous alloy powder with a resin, which serves as the insulator as well as the binder, are applicable for radio-frequency magnetic cores such as noise filters and smoothing choke coils.

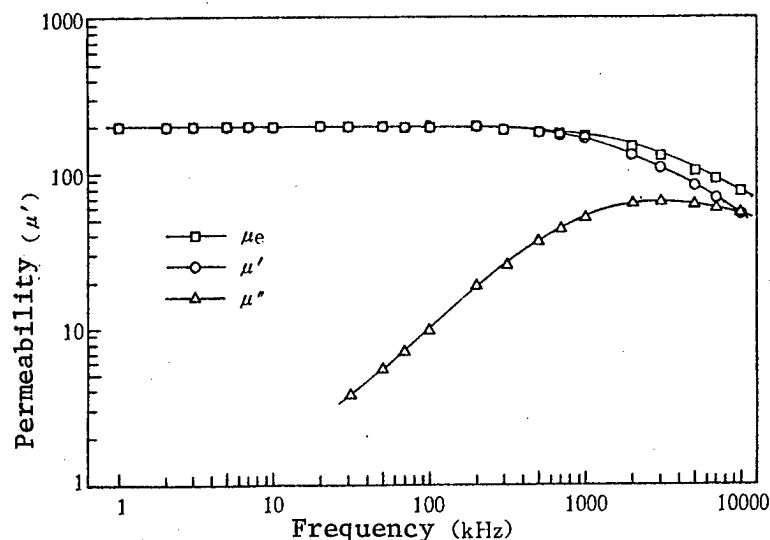


Figure 9. Plot of Frequency Against Permeability for Molded Cores Made From an Amorphous Alloy Powder and a Resin

Figure 9 shows the plot of permeability versus frequency for an amorphous resin molded core of the powder $(\text{Co} + \text{Fe})_{75}(\text{Si} + \text{B})_{25}$. The effective permeability stays approximately constant at 200 near the frequency of 1 MHz; this permeability value far surpasses those of pressed powder cores (dust cores), Sendust cores, and permalloy dust cores.

4.3 Amorphous Sheets

Because of their large aspect ratio, amorphous alloy powders such as those shown in Photos 1(a) and (b) [omitted] are anisotropy in shape, which provides them with an advantage magnetically. When spread and fixed over a film, they make an amorphous sheet. With each particle in contact with another, they may be made to exhibit characteristics like those of a board and be handled with extreme ease because needed quantities of the powder may be spread over the required area.

This type of sheet is applicable for magnetic shielding; sheets of high permeability and zero magnetostriction, in particular, are easy to cut and bend and are hardly affected by shape distortion and, hence, can be fixed to plastics, etc. with an adhesive agent without their characteristics deteriorating. Figure 10 plots the magnetic shielding effects for direct current. The method of measurement is based on $H_0 = 1\text{G}$ and involves the use of an amorphous sheet 200 mm by 200 mm. It is evident that the shielding effect grows with an increase in the weight of the powder per unit area. An isotropic silicon steel 0.5 mm thick (4 kg/m^2) subjected to the same measurement, in contrast, exhibits a very small H_0/H_i value of 6, verifying the very fine shielding effects of the amorphous sheet.

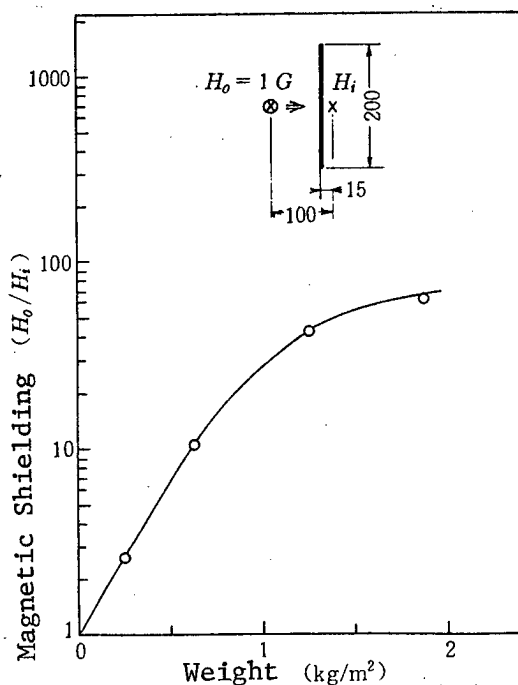


Figure 10. Plot of Magnetic Shielding Versus the Weight of the Amorphous Alloy Powder for the Amorphous Sheet

5. Conclusion

Features of amorphous alloy powders vary with grain diameter, and hence, the secondary processing of these powders involves an extremely wide range and complex details, on the other hand, this should provide a diverse range of applications. It is hoped that the present article spotlights potential needs for the powder, leading to further expansion of its applications.

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SENSOR TECHNOLOGY

DEVELOPMENT OF PHOTORESPONSIVE MATERIALS DISCUSSED

Tokyo SENSOR GIJUTSU in Japanese Jul 86 pp 44-46

[Article by Shigeo Tazuki and Tomibi Ikeda of Tokyo Institute of Technology]

[Text] The advent of a society with a highly sophisticated information network necessitates the development of a memory device with high capacity and high speed. The Ministry of International Trade and Industry (MITI), at this juncture, has taken up "photochemical reaction" as a subject for its Research and Development Project on Basic Technologies for Future Industries and set up a system to tackle this problem with the concerted efforts of the government, academic circles, and industries concerned. The special study "photochemical process" conducted by the Education Ministry also covers "the designing of raw materials for reciprocal photoresponses."

1. Prospect of Raw Materials for Optical Memory Elements and Problems Involved

Raw materials for optical memory elements, as are well known, have potential properties superior to those of other memory device materials in terms of speed and capacity for information processing. In particular, an optical memory of high density and high speed may be developed since a large number of signals may be carried on one single spot of a laser beam if the method of photochemical hole burning (PHB), whose principle was reported in the Soviet Union in 1974 and which was successfully performed at an IBM laboratory in the United States is used. Present optical memory devices have a memory density theoretically limited to 10^8 bits/cm², whereas PHB allows the density to rise to 10^{15} bits/cm². The response speed also improves drastically and access time shortens to a length comparable to those for ICs. PHB, nevertheless, has a long way to go before it can be put to practical application. Many problems remain to be solved; for example, the PHB phenomenon can occur only at ultra-low temperatures and the photochemical reaction involved in the formation of holes is not necessarily reversible.

The application of low molecular weight substances exhibiting reversible photochemical reactions as raw materials for optical recording is a long-standing idea; in particular, optical recording by means of photochromism has been explored extensively and involves the exposure of a material to lights of different wavelengths, thereby producing two stable states of the molecule which make writing, reading, and erasure of information possible.

This process is simpler than PHB. Examples of the molecules exhibiting reversible photochemical reactions which have been put to use to date are presented in Figure 1. One problem in the use of organic molecules for optical recordings is the lifespan of the material for repeating. Exposure to light produces some side reactions which diminish the number of repeatable cycles.

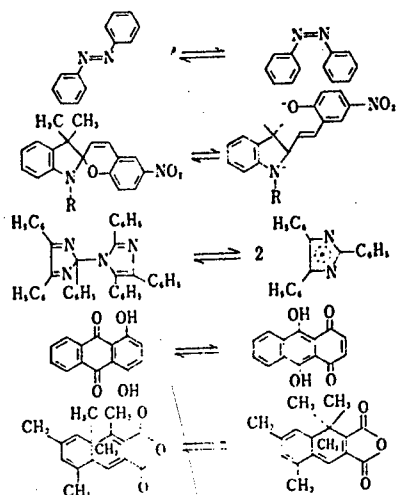


Figure 1. Molecules Capable of Reversible Photochemical Reaction

Inorganic materials are superior in terms of the number of repeatable cycles but inferior in their sensitivity to light response. The advantages of organic molecules, on the other hand, are that their structures may be changed and the arrangement of their atoms be controlled with comparative ease. Even some organic materials seem to be able to have up to 10^4 repeatable cycles, which is important in terms of stable recording.

The main feature of optical memory materials is the capability, in principle, to make multiwavelength recordings; this may be made sufficiently practical if the degree of wavelength resolution is upgraded by such means as using a chromophor with a narrow half width of the interval of absorption frequencies. Where practical application is concerned, response speed and S/N [sensitivity to noise ratio] are the dictating factors and the molecules shown in Figure 1 are sufficient for response speed. Azobenzene takes less than 10^{-7} seconds to cis-trans isomerize; and fulgide less than 10^{-9} seconds, as has been reported. Nevertheless, the problem is not so simple when the response speed of the entire device is concerned.

The problem involves reading sensitivity and how many molecules are needed for a response in order to provide sufficient S/N; in other words, how to amplify fine chemical reactions.

2. Upgrading Functions of Optical Memory Materials

An internal amplification device may have to be developed if optical memory materials are to become highly sensitive. Examples of the elements with an internal amplification function that convert optical signals are the retinal cells of the body. An intrinsic membrane protein with an optical receptor retinal, referred to as a rhodopsin, exists in the retinal cells of the vertebrate animal and plays a dominant role in the initial step to visual sensation. Upon the absorption of photons, the retinal undergoes cis-trans isomerization within 2.5×10^{-11} seconds. This local conformational change influences the opsin, to which the retinal is linked, thereby amplifying the optical signal. The amplification is carried out in such a way that the absorption of one photon produces hydrolysis of cGMP of over 10^5 molecules. The optical signal thus amplified is eventually converted to cell membrane electric potentials.

Such a sequence of processes for converting optical signals may generally be defined as "occurring in the device of a molecular agglomerate involving optical receptors and aiming at producing changes in the physical properties of the agglomerate by means of optical signals which serve as chemical triggers and, thereby, amplifying the optical signal." Though actual cases of successful internal amplification of optical signals by means of optical memory elements based on this principle have yet to be seen, research is being conducted.

Irie, et al., coupled azobenzene, spiropyrane, and other photoreactive molecules with the main chain or side chain of a polymer and systematically examined the change in the physical properties of the polymer upon its exposure to light. Where azobenzene is concerned, the distance between the two carbon atoms at the para position of the two benzene rings is 9.0 Å for the transform and 5.5 Å for the cis form and the dipole moments changed from 0.5 D to 3.1 D. Conversion between the two isomers is achieved by exposing them to light of different wavelengths. Figure 3 is the response to light of a polymer selected from among several coupled with azobenzene, which are listed in Figure 2. An exposure to light with a wavelength of 350-410 nm, the isomerization from trans to cis takes place accompanied by a lowering of the viscosity of the polymer; exposure to light with wavelengths of over 470 nm, in turn, produces reverse isomerization from cis to trans with the viscosity of the polymer solution reverting to its initial high level. Since the viscosity of a polymer solution represents a physical value reflecting the extension of the polymer chains in the solution, the above change implies that the trans-to-cis isomerization of the azobenzene joined to the main chain of the polymer is translated and amplified to the change in the conformation of the entire polymer (between the expansion and the contraction types). It has been verified by means of the laser flash photolysis method and the laser pulse light scattering method that the time required for optical cis trans isomerization of azobenzene is less than 10^{-7} seconds and for the conformational change of the relevant polymer 10^{-3} seconds.

Changes in the form of polymer chains resulting from optical isomerization of azobenzene have been reported also for polypeptides, to which azobenzene

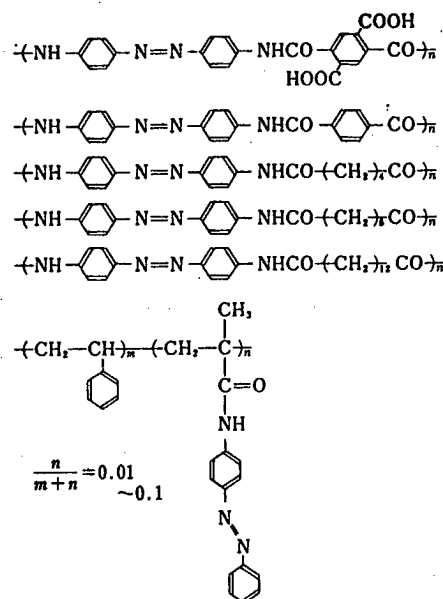


Figure 2. Photoreactive Polymers Involving Azobenzene

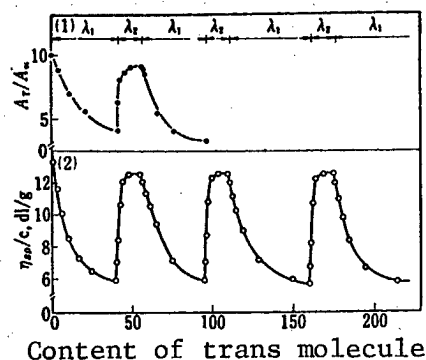


Figure 3. Response to Light of Polymers Involving Azobenzene in Mainchain

(1) Viscosity in N, N' dimethyl acetoamide solution

(2) Time in minutes

$\lambda_1 = 350 \sim 410 \text{ nm}$, $\lambda_2 = > 470 \text{ nm}$

is coupled to a side chain. Ciardelli, et al., joined azobenzene to the side chains of polyglutamic acid in various ratios and subsequently subjected the product to optical isomerization in an aqueous solution of trimethyl phosphate. They then proved by means of a circular dichronic (CD) spectra that the molecular association of the polypeptide had changed drastically.

The authors, in turn, have carried out their own laboratory research on the process of optical signal conversion based on a visual model which is to follow.

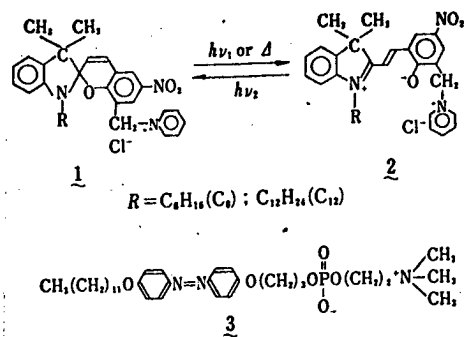


Figure 4. Amphiphiles With a Group Capable of Reversible Photochemical Reaction

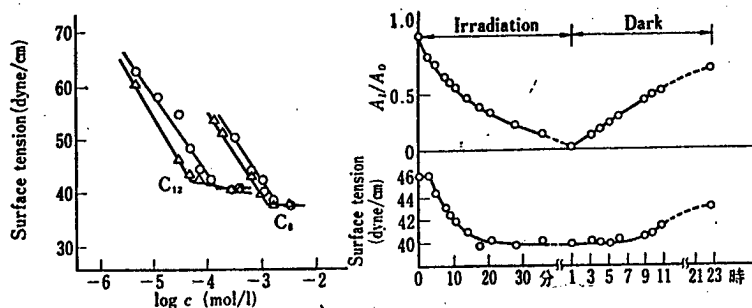


Figure 5. Surface Tension γ of an Amphiphile Incorporating a Spiropyrane Structure in Aqueous Suspension

- (1) Dependence of γ on concentration
- (2) Changes of γ resulting from photochemical isomerization ($2 \rightarrow 1$) and thermal isomerization ($1 \rightarrow 2$)

When an amphiphile of the cation type involving a spiropyrane structure near the polar group (1 of Figure 4) was suspended in water, the merocyanine type (2) was the more stable form with higher CMC (Figure 5(1)). Subsequent exposure to light of type 2 at a concentration range between the CMCs of 1 and 2 produced optical isomerization from 2 to 1 which, they noted, was accompanied by a nonlinear drop of the surface tension γ , as shown in (2) of Figure 5. The value of γ stayed nearly constant at a reaction rate of up to 20 percent. With further progress in optical isomerization, however, the value fell abruptly, suggesting that the suspension system had undergone a noncontinuous change in phase from free monomers to micelles.

With its polar terminal occupied by a substance similar to phosphatidylcholine, amphiphile 3 in Figure 4, when suspended in water, forms micelles of a disk type when the azobenzene group is in trans form, but those of a rod type when the substance is isomerized optically to cis form. When this process is pursued with light scattering intensity R_θ as a measurement, the value falls with trans-to-cis isomerization, and does so precipitously after a certain critical value is passed, as shown in Figure 6. This suggests that the morphological change from the disk to the rod type takes place rapidly after the critical value of R_θ is passed.

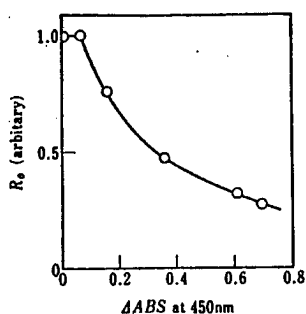


Figure 6. Changes of Light Scattering Intensity for Amphiphiles Involving Azobenzene in Aqueous Suspension (the Abscissa Indicates Contents of the Cis Form)

The above morphological change induced by light relates nonlinearly to the progress of the chemical reaction involved; a very fine photochemical reaction in a limited range produces a major change in the morphology of the system and thus acts as, say, a physical amplifier. In principle, a high sensitivity, or high S/N, and energy conservation may materialize by applying optical memory elements of the internal amplification type involving physical amplification such as the kind mentioned above.

Nevertheless, it is still a long way from practical application. The first question to be resolved is how to induce a physical amplification process in a solid system. One answer is the use of liquid crystal. Following the pioneering research made by Sackmann, Suzuki, Nakamura, et al., have recently reported on their research on information recording using phase changes induced by photochemical changes of azobenzene and spiropyran in liquid crystal. One can expect high sensitivity from this process since phase transition from solid phase to liquid crystal is abrupt and involves major changes in physical properties.

Available for the reading of optical information are not only changes in the extinction coefficient but also all other changes in physical properties, e.g., refraction index, angle of rotation, electrical conductance, and dielectric constant. All these make photochromic materials in the wider sense of the term. The change in the degree of rotation involved which is equivalent to the one for the photomagnetic material--which, however, involves the reading of transmitted light--is of particular interest with its basic research already embarked upon.

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